Mechanistic Investigation into the Conversion of Methanol to Hydrocarbons by Zeolite Catalysts

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ABSTRACT

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Zhaohui Liu

Catalytic conversion of methanol to hydrocarbons (MTH) provides an alternative route to the production of fuels and important industrial chemicals that are currently mainly produced from the refinery of petroleum. The ability to control the product distribution of MTH according to the demands of specific applications is of crucial importance, which relies on the thorough understanding of the reaction pathways and mechanisms. Despite the significant research efforts devoted to zeolite-catalyzed MTH, it remains a challenge to establish a firm correlation between the physicochemical properties of zeolites and their catalytic activity and selectivity. In this dissertation, we designed a series of experiments to gain fundamental understanding of how the structural and compositional parameters of zeolites influence their catalytic performances in MTH. We investigated different types of zeolites, covering large-pore Beta, medium-pore ZSM-5, and small-pore DDR zeolites, and tune their crystallite size/diffusion length, hierarchical (mesoporous) structure, and Si/Al ratio (density of acid sites) by controlled synthesis or post-synthesis treatments.
The influence of mesoporosity of a zeolite catalyst on its catalytic performance for MTH, with zeolite Beta, was first investigated. The shorter diffusion length associated with the hierarchical structure results in a lower ethylene selectivity but higher selectivity towards C_4-C_7 aliphatics. Then we investigated the correlation between the Al content and the ethylene selectivity by ZSM-5 zeolites with similar crystal sizes but varied Si/Al ratios. We realized that ethylene selectivity is promoted with the increase of aluminum content in the framework. These two observations can be explained by the same mechanistic reason: the ethylene selectivity is associated with the propagation degree of the aromatics catalytic cycle and essentially determined by the number of the acid sites that methylbenzenes would encounter before they exit the zeolite crystallite. Last we explored how to maximize the propylene selectivity by tuning the physicochemical properties of DDR zeolites. Due to the confined pore space in DDR, the propagation of olefins-based catalytic cycle can be preferentially promoted in a tunable manner, which cannot be realized with zeolites having larger pores. Thus, the propylene selectivity increases with increasing the Si/Al ratio and decreasing the crystallite size.
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Things will be totally different if without the invaluable support and help from many individuals to whom I would like to express my most sincere gratitude here.

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<tr>
<td>1D</td>
<td>one-dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>three-dimensional</td>
</tr>
<tr>
<td>DME</td>
<td>dimethyl ether</td>
</tr>
<tr>
<td>HCP</td>
<td>hydrocarbon pool</td>
</tr>
<tr>
<td>HeptaMB⁺</td>
<td>heptamethylbenzenium cation</td>
</tr>
<tr>
<td>HMMC</td>
<td>hexamethylenecyclohexadiene</td>
</tr>
<tr>
<td>HTI</td>
<td>hydrogen transfer index</td>
</tr>
<tr>
<td>IZA</td>
<td>international zeolite association</td>
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<tr>
<td>MTA</td>
<td>methanol-to-aromatics</td>
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<tr>
<td>MTG</td>
<td>methanol-to-gasoline</td>
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<td>MTH</td>
<td>methanol-to-hydrocarbons</td>
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<tr>
<td>MTO</td>
<td>methanol-to-olefins</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>MTP</td>
<td>methanol-to-propylene</td>
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**Chapter 2:**

<table>
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<tbody>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
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<tr>
<td>DFT</td>
<td>density functional theory</td>
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<tr>
<td>EELS</td>
<td>electron energy loss spectroscopy</td>
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<tr>
<td>FIB</td>
<td>focused ion beam</td>
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<tr>
<td>FID</td>
<td>flame ionization detector</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<tr>
<td>GC</td>
<td>gas chromatography</td>
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<tr>
<td>HAADF</td>
<td>high-angle annular dark field</td>
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<tr>
<td>ICP-OES</td>
<td>inductively coupled plasma-optical emission spectroscopy</td>
</tr>
<tr>
<td>MAS</td>
<td>magic-angle spinning</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>STEM</td>
<td>scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
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TGA  thermogravimetric analysis
TPD  temperature-programed desorption
WHSV weight hourly space velocity
XRD  X-ray diffraction

Chapter 3:

2,2-dmb  2,2-dimethylbutane
BET  Brunauer–Emmett–Teller
DME  dimethyl ether
ICP-OES  inductively coupled plasma-optical emission spectroscopy
MBs  polymethylbenzenes
MSD  mass selective detector
SEM  scanning electron microscopy
TEM  transmission electron microscopy
TPV  total pore volume
XRD  X-ray diffraction
### Chapter 4:

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<tr>
<td>ADA</td>
<td>adamantylamine</td>
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<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>inductively coupled plasma-optical emission spectroscopy</td>
</tr>
<tr>
<td>MTO</td>
<td>methanol-to-olefins</td>
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<tr>
<td>P/E</td>
<td>propylene to ethylene ratio</td>
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<tr>
<td>SDA</td>
<td>structure directing agent</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>TPD</td>
<td>temperature-programed desorption</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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### Chapter 5:

<table>
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<tr>
<td>BASs</td>
<td>brønsted acid sites</td>
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<tr>
<td>BZ</td>
<td>benzene</td>
</tr>
<tr>
<td>CP</td>
<td>2, 3-dimethyl-2-cyclopenten-1-one</td>
</tr>
<tr>
<td>ET</td>
<td>ethylene</td>
</tr>
<tr>
<td>HPLC</td>
<td>high pressure liquid chromatography</td>
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PMBs  polymethylbenzenes
TGA  thermogravimetric analysis
UFF  universal force field
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Chapter 1: Introduction

Recently, the fast growth of global population and the rapid expansion of industrial production have been increasing the demand on energy. Nowadays, global energy is mainly obtained from the combustion of fossil fuels.\textsuperscript{1-3} Considering the growing energy request with the dwindling supply of crude oil, many alternative energy sources, such as the solar energy,\textsuperscript{4-5} wind,\textsuperscript{6} and biomass\textsuperscript{7-9} have attracted much attention for the increasing usage. The renewable energy sources are very promising to meet our urgent energy request due to their sustainability, cleanliness and inexhaustibility. However, the instability and intermittence of these renewable energy sources still limit their widespread applications in our life now.

The process of methanol-to-hydrocarbons (MTH) over solid acidic zeolite catalyst was first discovered by the Mobil Company in 1976,\textsuperscript{10} and commercialized to produce gasoline at New Zealand in 1985.\textsuperscript{11} This MTH reaction has the ability to produce a variety of different hydrocarbons, and its feedstock, methanol (or dimethyl ether), can be produced in a massive scale from coal, biomass and natural gas via a syngas intermediate process.\textsuperscript{12-14} So, the conversion of methanol-to-hydrocarbons, as an alternative nonpetroleum process to supply our world with fuels and chemicals, has attracted much attention in recent years.\textsuperscript{15-18}

In this introductory chapter, I will show some fundamental insights on the conversion of methanol-to-hydrocarbons, and discuss the scope of this dissertation. I begin with a
short introduction on the MTH conversion in Section 1.1. From this beginning, the mechanism of MTH conversion is discussed in Section 1.2. Then, the elementary sub-reactions which occur within MTH conversion are illustrated in Section 1.3. Following that, Section 1.4 discusses the effects that influence the product distribution in MTH conversion. And at the final part of the introduction, Section 1.5 talks about the lifetime of zeolite during the MTH reaction. Based on this introduction, the scope of this dissertation is presented in Section 1.6 at the end of this chapter.

1.1 The process of methanol-to-hydrocarbons (MTH) conversion

The MTH conversion has attracted considerable attention in the past few decades, because it was believed to be a new way to produce fuels and chemicals independent of petroleum-based synthetic routes (as shown in Figure 1.1). According to the product distributions, MTH reaction can be classified into the following categories, methanol-to-olefins (MTO),\textsuperscript{19-21} methanol-to-gasoline (MTG),\textsuperscript{11} methanol-to-propylene (MTP)\textsuperscript{22-24} and methanol-to-aromatics (MTA)\textsuperscript{25}. The details of this reaction will be illustrated in the following sections.

The catalyst used for the MTH process is zeolite, which is a class of crystalline microporous inorganic materials (silicates, aluminosilicates, titanosilicates, aluminophosphates, etc.) with ordered cavities and channels of molecular dimensions (0.3—1 nm).\textsuperscript{26-32} The uniform microporous structures of zeolites offer the “molecular sieve” function, accounting for their unique size- and shape- selectivity in adsorption,
separation, and catalysis applications. The primary building blocks of zeolite are TO$_4$ tetrahedra with Si$^{4+}$ or Al$^{3+}$ at the center and oxygen at the corner. The tetrahedra with negative charged (AlO$_4$) will make the zeolite possess acidity for the catalysis application. The pore sizes of zeolites contribute to the shape or product selectivity in reactions, by restricting the diffusion of substances or formed species to the internal channels of zeolite or the external systems. A simple classification of pore size is based on the number of T atoms which forms the window of zeolite; typically they are 12-, 10-, and 8-ring, referring to large, medium, and small pore zeolite. In Table 1.1, we show some typical topologies of zeolite used in the MTH conversion.

**Figure 1.1.** The process of methanol-to-hydrocarbons (MTH) conversion.$^{17}$

![Figure 1.1.](image-url)
Table 1.1 Typical topologies of zeolite used in MTH conversion.\textsuperscript{15}

<table>
<thead>
<tr>
<th>Topology</th>
<th>Material</th>
<th>Channel structure</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEA</td>
<td>beta</td>
<td>3D, 12-ring</td>
<td>Si/Al = 8–25</td>
</tr>
<tr>
<td>MFI</td>
<td>ZSM-5</td>
<td>3D, 10-ring</td>
<td>Si/Al = 10 – ∞</td>
</tr>
<tr>
<td>TON</td>
<td>ZSM-22</td>
<td>1D, 10-ring</td>
<td>Si/Al = 30</td>
</tr>
<tr>
<td>CHA</td>
<td>H-SAPO-34, SSZ-13</td>
<td>3D, 8-ring</td>
<td>Al(50)P(30–45)Si(20–5)</td>
</tr>
<tr>
<td>DDR</td>
<td>Sigma-1</td>
<td>2D, 8-ring</td>
<td>Si/Al = 20–200</td>
</tr>
</tbody>
</table>

Hierarchically structured zeolites, which combine the merits of microporous zeolites and mesoporous materials to offer enhanced molecular diffusion and mass transfer without compromising the inherent catalytic activities and selectivity of zeolites (as shown in the schematic Figure 1.2), have attracted much attention recently. Significant efforts have been expended on the preparation of hierarchical zeolites, which can be classified into a post-treatment method and a direct-synthesis route.\textsuperscript{26, 33–39} Post-treatment methods, such as steaming, acid (or base) leaching, and chemical treatment, have been used to create mesopores in zeolites.\textsuperscript{34, 40–47} These processes are eco-unfriendly and only produce poorly defined mesopores. By comparison, direct synthesis of hierarchical zeolites through the “templating route” allows more precise control of the mesoporosity and also better integrity of the zeolite structures by avoiding desilication or dealumination.\textsuperscript{48}
1.2 The mechanism of MTH conversion

The product distributions are generally determined by the reaction conditions and the structure of zeolites. In order to achieve the product distribution control, many efforts have been devoted to clearly and deeply understanding the mechanism of the MTH reaction. The mechanistic study, which is of utmost importance to tailor the product selectivity, has been the central part in MTH research for over 30 years.\textsuperscript{15-17}

1.2.1 The induction period

It was early thought that MTH goes through an autocatalytic process in which the concentration of hydrocarbons increases with the subsequently increased rate of methanol or DME conversion.\textsuperscript{49} This process is also known as the induction period...
during which the organic-free zeolite catalyst is transferred to a working catalyst. Qi et al. unraveled the reaction behavior of MTH conversion in the induction period over HZSM-5 zeolite at low temperatures. In this research, they found that the induction period, which is usually very short and hard to be trapped, could be expanded to more than 2 h at a low temperature (at 255 °C and lower). And most importantly, they claimed that the accumulation of hydrocarbons is the rate-determining step, and thus the addition of aromatics with methanol could shorten the induction period, and they even further calculated that per 276 unit cells of ZSM-5 (Si/Al = 19) needs 1 toluene molecule to start the autocatalysis reaction.

During the induction period of the MTH conversion, the most important and also difficult question is how the first C-C bond is formed. Many different possible routes (over 20 possible mechanisms) for the formation of first C-C bond from methanol or DME have been proposed till now, such as carbocations, carbenes, acetate species, and free radicals. However, the clear mechanism of the first C-C bond formation is not reach in an agreement and still under debate now. Furthermore, a direct C-C coupling route requires the activation of a C-H bond, and it has been demonstrated that the activation energy barriers for the direct C-C formation from methanol molecules are very high (~200 kJ mol⁻¹), tested by Lesthaeghe et al. via ONIOM methods. Therefore, an indirect hydrocarbon pool mechanism has then been widely accepted and deeply investigated.
1.2.2 Hydrocarbon pool mechanism

Dahl et al. first proposed a “hydrocarbon pool” mechanism during MTH conversion. As shown in Figure 1.3, in this mechanism methanol forms an active pool of \((\text{CH}_2)_n\) species in zeolite pores in which methanol reacts with the species and products (light olefins, alkanes, and aromatics) are formed as well.\(^{53}\) Song et al. demonstrated that methylbenzenes are active species in the “hydrocarbon pool” during the MTO reaction. In their work, they found that the conversion of methanol was only 14% in fresh catalyst, but when the catalyst was pretreated to form methylbenzenes the conversion could achieve nearly 100% in the second methanol pulse.\(^{54}\) By co-reaction of \(^{13}\text{C}\)-Methanol and \(^{12}\text{C}\)-benzene in Beta zeolite, Kolboe et al. directly observed the incorporation of \(^{12}\text{C}\) atoms into both gaseous products and retained species, which provided further evidence for the hydrocarbon pool mechanism that methylbenzenes are the active hydrocarbon intermediates for the products formation during the MTH conversion.\(^{55}\)

![Figure 1.3](image)

Figure 1.3. A “hydrocarbon pool” mechanism in MTH conversion (as claimed in reference\(^{53}\)).
1.2.3 Dual cycle mechanism

As a further development of the “hydrocarbon pool” mechanism, Bjorgen and co-workers revealed that two kinds of active hydrocarbon intermediates are at work during the MTH process over ZSM-5 zeolite. By isotopic switching experiments in which $^{12}\text{C}$ methanol feed is switched with $^{13}\text{C}$ methanol feed in the steady state reaction, they found that the content of $^{13}\text{C}$ incorporated in ethylene closely matched that in methylbenzenes, while the content of $^{13}\text{C}$ incorporated in propylene and higher olefins matched each other (Figure 1.4a). This is the so called dual cycle mechanism (as shown in Figure 1.4b), in which the aromatics-based active intermediates and olefin-based hydrocarbon pool species repeatedly undergo methylation, dealkylation or β-scission reactions to produce the complex hydrocarbons.

![Figure 1.4](image)

**Figure 1.4.** (a) Total $^{13}\text{C}$ content in the effluent compounds during MTH conversion on ZSM-5. (b) Proposed dual cycle concept for the conversion of methanol over ZSM-5.
The complicated product distributions seem to be clearly explained by the emergence of the dual catalytic cycle mechanism. For example, ZSM-22 has one-dimensional non-interacting 10-member-ring channels that are too small to form polymethylbenzenes intermediates, which suppress the aromatics-based cycle, and thus the olefin-based cycle is relatively promoted in the conversion process, resulting in high selectivity for branched C₅⁺-fraction alkenes. In ZSM-5 samples with different diffusion length, the ethylene and total olefin selectivity increase with the effective crystallite size, owing to the promoted propagation of the aromatics-based cycle as a result of prolonged intra-crystalline residual time of methylbenzenes. Additionally, increasing the methanol partial pressure could favor the hydrogen transfer process, and thus enhance the aromatics-based cycle with a high selectivity toward ethylene. Furthermore, many computational methods have recently been developed to support the “dual cycle” mechanism.

With various investigations on the ‘dual cycle’ concept, scientists reached a statement of agreement as shown in Table 1.2: in aromatics-based cycle, the main terminal products are ethylene and methane, so they can be used as the indicators of this catalytic cycle, and the active species are methylbenzenes; in the olefin-based cycle, the main indicators are C₄–C₇ aliphatics, and the active species are olefins. Propylene is produced from both cycles and consumed in the olefin-based cycle. And more importantly, these two cycles compete for the catalytic sites during the reaction process,
which can be applied to adjust the relative propagation of a certain cycle to regulate the product selectivity.\textsuperscript{17, 64-65}

**Table 1.2:** The indicators and active species claimed in the dual cycle mechanism.\textsuperscript{17, 64-65}

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Active species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics-based cycle</td>
<td>$C_2^*$ and CH$_4$</td>
</tr>
<tr>
<td>Olefin-based cycle</td>
<td>$C_4$–$C_7$ aliphatics</td>
</tr>
</tbody>
</table>

1.3 **Elementary sub-reactions within MTH conversion**

According to the dual cycle mechanism, there are six major elementary sub-reactions which may occur within MTH: olefins methylation and cracking, hydrogen transfer, cyclization, and aromatics methylation and dealkylation. Knowing the kinetics and mechanisms of these chemistries can help us to learn the effects on the product distribution in MTH conversion.

1.3.1 **Olefin methylation and cracking**

Olefin methylation is the way that methyls (from methanol or dimethyl ether (DME)) incorporate into lower olefin hydrocarbons, to form higher olefins. Two proposed mechanisms for olefin methylation are claimed in the literature: one is the co-adsorbed mechanism, which means that methanol (or DME) and one olefin are co-adsorbed on one acidic site and then react in one concerted step; the other is a stepwise mechanism,
in which methanol (or DME) forms a methoxide first and which then reacts with the olefin.\textsuperscript{17}

Much experimental and computational research has been devoted to the methylation of C\textsubscript{2}–C\textsubscript{4} olefins on various kinds of zeolites (ZSM-5, BEA, MOR and FER).\textsuperscript{66-71} These studies on the kinetics of olefins’ methylation showed that this reaction has a zero-order dependence on methanol or DME and a first-order dependence on the pressure of olefin.\textsuperscript{66-71} This relationship between the olefin methylation and methanol or DME means that the surface of the solid catalyst is saturated by these methylating agents (methanol or DME).\textsuperscript{17} Another very important message needs to be noted is that the activation barrier decreases and the olefin methylation rate accordingly increases with the increase of olefin’s size, which is related to the degree of substitution on the double bond. And thus, during the MTH conversion, highly branched aliphatics are favored because the most substituted carbenium ions are promoted as the reaction intermediates.\textsuperscript{66-71}

Olefin cracking as an effective route to produce light olefins during MTH conversion was first proposed by Dessau and LaPierre,\textsuperscript{72-73} and it was considered as an important route to increase the production of propylene in Lurgi’s methanol-to-propene (MTP) process over ZSM-5 zeolite.\textsuperscript{17} The olefin cracking process first requires the protonation of one higher olefin to form an active alkoxide species, and then the active alkoxide produces one smaller olefin and one smaller alkoxide followed by a β-scission process. Finally, this
smaller alkoxide desorbs from the catalytic site with one olefin formed and a proton left to regenerate the catalytically acidic site.

The rate of olefin cracking compared to olefin methylation is critical in determining the product distribution for MTH. For example, when olefin cracking is relatively faster than methylation, the product selectivity will be rich in lower olefins. In an opposite way, when olefin cracking is slower than the olefin methylation, higher olefins are promoted, which may eventually form aromatics by cyclization. To elucidate the rates of β-scission on different zeolites could help us to learn about the fraction of olefins in the products.\textsuperscript{74-76} For example, it was found that the rate of β-scission is generally about 40 times slower than olefin methylation, but the β-scission for a C\textsubscript{8} isomer (344T2P) is nearly twice as fast as the olefin methylation on Beta zeolite.\textsuperscript{74} Additionally, it was claimed that the cracking rates for olefins increase with increasing the carbon number with the ZSM-5 catalyst.\textsuperscript{76} Generally speaking, to understand the kinetics of olefin methylation and cracking can help us to link the dual-cycle mechanism to the product distribution during MTH conversion.

1.3.2 Hydrogen transfer

The hydrogen transfer reaction is a bimolecular process in which the proton atom is transferred between an active alkoxide and a cyclic alkene or alkane. As shown in the mechanistic scheme (in \textbf{Figure 1.3b}), it behaves like a bridge which acts as a connection between the olefin-based catalytic cycle and the aromatics-based catalytic cycle during the MTH conversion. The higher olefins will react to form aromatic species via this
process with the release of alkanes. So, paraffins are usually termed as hydrogen transfer index (HTI), because they are prevalently accompanied by the formation of aromatics, which is a stoichiometric requirement for hydrogen-redistribution pathways during zeolite-catalyzed hydrocarbons conversion. And thus, the HTI can be used to refer to the degree of the formation of aromatics species, and subsequently the propagation of aromatics-based catalytic cycle (another factor is the diffusion of the formed aromatics).

1.3.3 Cyclization

Cyclization is usually related to the process of aromatization because the cycloalkanes and cycloolefins are not stable products in MTH and are then quickly dehydrogenated to form aromatics. Two possible routes to olefin cyclization and aromatization were proposed. In one route, high olefins first dehydrogenate to form dienes and trienes and then undergo a cyclization process to form aromatics. In the other route, the olefins form cycloalkanes first and subsequently dehydrogenate to aromatics. The process of cyclization and aromatization is also a connection between the olefin-based cycle and aromatics-based cycle in MTH conversion.

1.3.4 Aromatics methylation and dealkylation

Aromatics, mainly polymethylbenzenes, along with the olefins mentioned above, act as scaffolds for the methylation and dealkylation process for the formation of the complex products during the MTH catalysis. Similar to the olefin methylation process, two
proposed mechanisms were claimed for aromatic methylation, i.e. co-adsorbed mechanism and stepwise mechanism.\textsuperscript{17}

Aromatic dealkylation is a very important process acting as a route to olefins production during the MTH conversion. As shown in Figure 1.5, two different proposed mechanisms have been stated for the aromatic dealkylation: the side-chain mechanism and the paring mechanism.\textsuperscript{81} This scheme can clearly show the details of the aromatics methylation and dealkylation processes, and the mainly products (ethylene and propylene) from it.

The process of the paring mechanism is initiated by the gem-methylation of one methylbenzene, resulting in ring contraction (with 5-ring organic species formed). The formed alkyl substituent, in turn, can crack to form ethylene or propylene.\textsuperscript{52-84} The cyclopentenyl cations in this process were confirmed by the IR and NMR techniques over ZSM-5 zeolite.\textsuperscript{83-84} In the side-chain mechanism, the starting point is also a gem-methylation of methylbenzene, which results in an elimination of one methyl hydrogen, with the formation of an exocyclic double bond, which can undergo side chain methylation.\textsuperscript{81, 85-86} This side chain, which cracks to produce light olefins, behaves in an general way for the products in the MTH process. With the aid of GC-MS and ssNMR technologies, Li and coworkers directly observed the Hexamethylene cyclohexadiene (HMMC) species and Heptamethylbenzenium cation (heptaMB\textsuperscript{+}) in SAPO type zeolite during the MTH reaction process, which shows direct evidence of this side-chain mechanism.\textsuperscript{85}
Figure 1.5. A representation of the paring and side-chain methylation mechanism for olefin elimination from Hexamethylbenzene with the zeolite represented as Z-H or Z− in its protonated or deprotonated form, respectively.\textsuperscript{81}

1.4 Effects on the product distribution of MTH conversion

Product distribution and transition-state shape selectivity in MTH conversion have been widely reported.\textsuperscript{52-53} Many factors have a remarkable influence on the mechanism of MTH conversion and thus on the product distribution, and mostly they are the feed identity, reaction conditions, structure of zeolites on topology and textural properties. In this part, I will present the details on how these factors affect the product selectivity during the MTH process.
1.4.1 Co-feeding active intermediate species

Based on the dual cycle mechanism, methylbenzenes are the active species in the aromatics-based cycle while high olefins are the active species for the olefin-based cycle. When the amount of one certain active species is increased by co-feeding route with the feedstocks, the according reaction cycle will subsequently be enhanced with a promoted selectivity toward the products in this cycle.

For example, Ilias et al. revealed that when they co-fed certain amounts (0–4 kPa) of toluene in the feedstock during the MTH conversion at 275 °C over ZSM-5, the selectivity toward ethylene and aromatics increased from 14.5 to 18 C% and 7.1 to 33.7 C% respectively, while the selectivity of C₄–C₇ aliphatics decreased from 42.8 to 16.9 C%. Sun et al. also found that with the increasing concentration of p-xylene in methanol, the selectivity of methane, ethylene and aromatics are promoted, while those of C₄–C₇ aliphatics are decreased (as shown in Figure 1.6). Specifically, the selectivity toward ethylene (3.5–14 C%) and aromatics (0.8–3.6 C%) increased approximately 4 times, when the feedstocks changed from pure methanol to methanol co-fed with 4 C% p-xylene. The mechanistic reason was attributed to the enhanced aromatics-based catalytic cycle and suppressed olefin-based cycle with the xylene co-fed. Interestingly, they also noted that the addition of a small concentration of C₃–C₆ olefins to methanol cannot selectively suppress the aromatics-based catalytic cycle. Recently, Khare et al. further revealed that co-feeding acetaldehyde (1–4 C%) with dimethyl ether (DME) and methanol resulted in a monotonic increase on the selectivity
toward ethylene (9.3–15 C% over conventional ZSM-5 and 1.4–6.4 C% over diffusion-free ZSM-5) and methylbenzenes (4.9–7.8 C% over conventional ZSM-5 and 2.6–5.3 C% over diffusion-free ZSM-5). Even though acetaldehyde is not the active species in the aromatics-based cycle in the MTH reaction, it will undergo multiple aldol-condensation reactions to form aromatics which in turn enhance this catalytic cycle.  

Figure 1.6. The influence of co-feeding p-xylene on the product selectivity in terms of methane (a), ethylene and propylene (b), C₄–C₇ aliphatics (c), C₂–C₄ paraffins and aromatics (d).  

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1.4.2 Reaction conditions

According to the abovementioned kinetics study on the elementary sub-reactions in the MTH reaction, the reaction conditions (temperature and pressure) have much influence on the rates of the sub-reactions as they have different kinetic orders and energies for activation, and thus are able to tailor the product selectivity. For example, by operando UV-vis spectroscopy, Weckhuysen’s group revealed that 1-methylnaphthalene plays as a deactivating species at 350 °C in the MTH reaction over DDR zeolite, whereas it is an active species at a higher temperature (450 °C). They also found that the major active hydrocarbon pool (HCP) species during the MTO reaction on CHA zeolites (i.e. SSZ-13 and SAPO-34) differ at different reaction temperatures. At low reaction temperatures (i.e., 300–350 °C) the active species are methylbenzenes, while at higher reaction temperatures (i.e., 350–500 °C) methylated naphthalene becomes the main active intermediate. However, Qi et al. found that naphthalene can also act as an active HCP species at low temperature (290 °C) in ZSM-5 zeolite. Moreover, Yarulina et al. revealed that the change of reaction temperatures from 380 °C to 475 °C changes the ethylene-to-propylene ratio in the products from 0.5 to 1.6 during the MTO reaction over the Sigma1 catalyst (Si/Al = 157). And also the yield of butenes could reach a maximum of 14 % at 380 °C while it cannot exceed 5 % at 475 °C.

Another representative example to illustrate the effect of reaction conditions on the product distribution is the research work from Bhan’s group on the pressure of methanol (as shown in Figure 1.7). When they adjusted the pressure of methanol from
0.6 to 52.5 kPa during the methanol-to-hydrocarbons catalysis on ZSM-5 at 400 °C, they found that methylbenzenes and ethylene selectivities show monotonically increasing trends, from 0.1 to 5.9 %C and from 1.5 to 9.8 %C, respectively. While, the selectivity to propylene shows a commensurate decreasing trend from 41.8 to 28.7 %C, and P/E shows a 9-fold decrease from 18 to 2. They stated the reason as that high pressure of methanol favors the hydrogen transfer process, which produces aromatics and thus enhances the propagation of the aromatics-based cycle in MTH conversion.\textsuperscript{61}

![Figure 1.7](image_url)

**Figure 1.7.** (Left) Selectivity and methanol (+ DME) conversion on carbon basis (%C), (Right) Ethylene and 2MBu (sum of 2-Methyl-2-butene and 2-Methylbutane) selectivities on carbon basis (%C) and their ratio. \textsuperscript{61}
1.4.3 Structure of zeolites

According to the international zeolite association (IZA) database, about 200 different types of zeolite have been found. The topologies (channels and cavities), compositions (Si, Al, P, Ti et al.) and morphologies (crystal dimensions and porosity) of zeolites are varied very much, and have remarkable influence on their catalytic performances during the MTH conversion.

First, the topology of zeolite plays an important role on the mechanism of MTH conversion. For example, the MFI structured ZSM-5 (a 3-dimensional 10-ring structure with pore sizes of 5.1 × 5.5 and 5.3 × 5.6 Å) was demonstrated to produce a mixture of alkanes, alkenes and a major part of aromatics. While the CHA structured SAPO-34 (a 3-dimensional cage structure with window openings of 3.8 × 3.8 Å) was shown to produce mainly C₂ – C₄ alkenes, at the same reaction conditions. More specifically, the main active hydrocarbon pool in MTH reaction are different between different morphologies of catalysts, for Beta zeolite, Hexamethylbenzene and Pentamethylbenzene were observed as the major active reaction intermediates, favoring the formation of propylene and butenes, while in ZSM-5, the active intermediates were found to be restricted to Xylene and Trimethylbenzenes, which favors ethylene and propylene.

The textural properties of zeolite are another important factor on the mechanism of MTH conversion. Bhan’s group systematically investigated the effect of crystallite size on product selectivity in MTH conversion over ZSM-5. As the results shown in Figure 1.8, the selectivity of ethylene is promoted with the increase of the particle size, but the C₄ -
C₇ aliphatics is suppressed at the same time. When ZSM-5 particle was coated with a SiO₂ shell, they found the same trend on the selectivity as the increase of the particle size. Their results showed that larger “effective crystallite size” favors the aromatics-based cycle to give a higher light olefins selectivity, because of the prolonged intra-crystalline residual time of the active methylbenzenes (as clearly shown in the cartoon figure of Figure 1.8). And also, Zhao et al. found that in high-Si structured Beta zeolite, the olefin-based mechanism can dominate the MTP reaction and contributes to the formation of propene and higher olefins, leading to a high propylene selectivity of 58.3%. Very recently, Gascon’s group at KAUST revealed that the modification of ZSM-5 with alkaline-earth metal reduces the number of Brønsted acid sites in the catalyst, and thus suppresses the propagation of the aromatics-based cycle, while alkene methylation and the propagation of the olefin-based cycle can still continue. And finally, this alkaline-earth metal modified ZSM-5 leads to a higher propylene selectivity and a lower ethylene selectivity than the pure ZSM-5.

Figure 1.8. Cartoon figure (left) and experimental data (right) illustrate the influence of the diffusion length on the products selectivity in MTH conversion over ZSM-5 zeolite.
1.5 Lifetime of the catalyst during MTH conversion

Of equal importance with the activity/selectivity of a catalyst is its lifetime. Like many other hydrocarbon reactions, MTH conversion is accompanied by the formation of coke, which causes gradual deactivation of the catalyst.\textsuperscript{96-100} Coke is complex in composition, mainly consisting of various polycyclic aromatics with broad mass distributions. These aromatics are formed and then evolve throughout the entire reaction process with a close correlation to reaction conditions.\textsuperscript{101-104}

Hierarchically structured zeolites, which combine the merits of microporous zeolites and mesoporous materials to offer enhanced molecular diffusion and mass transfer, are recognized as effective catalysts with elongated lifetimes in MTH conversion. The superior catalytic performances of mesoporous zeolites are usually attributed to the fact that the mesopores promote molecular diffusion, leading to slower coke formation and thus better accessibility to the catalytic active sites.\textsuperscript{96, 105-107} As investigated by Kaskel et al,\textsuperscript{96} mesoporous ZSM-5 showed a longer lifetime than microporous ZSM-5 during the MTH reaction. They claimed the reason was that the mesoporous catalyst has less diffusion restraints, and thus the whole particle can contribute to the reaction, while only the outer sphere of the microporous particle is useful as the coke easily blocks the interior part of the catalyst. Ryoo and coworkers also found that the as-synthesized hierarchically structured ZSM-5 nanosheets exhibited about a 5-fold longer lifetime than the conventional ZSM-5 catalyst in MTH conversion, and they attributed the superior performance of the hierarchical ZSM-5 to the high external surface area.\textsuperscript{105} Sun \textit{et al}.\textsuperscript{106}
used an organosilane surfactant as the mesoporogen to fabricate a hierarchical porous SAPO-34 successfully, and this catalyst showed an excellent performance in MTO reactions with a remarkably prolonged catalyst lifetime and enhanced selectivity of ethylene and propylene compared to the conventional microporous SAPO-34. Also, Wang et al.\textsuperscript{107} synthesized a spherical self-assembly of SAPO-34 nanosheets by combined usage of a quaternary ammonium-type organosilane surfactant as the mesopore director and diethylamine as the microporous template, and then they further demonstrated that the SAPO-34 zeolite with a hierarchically porous structure displayed a remarkable lifetime and a high yield of light olefins.

Recently, Müller et al. investigated the coke formation and deactivation pathway on ZSM-5 during the conversion of methanol to olefins in a novel method.\textsuperscript{100} By comparing the deactivation behavior of the catalyst in plug-flow and fully back-mixed reactors, they concluded that, in the initial stage of the reaction, high local methanol concentrations induce the formation of oxygen (O)-containing carbon species that strongly adsorb on the Brønsted acid sites, causing a rapid deactivation of the catalyst (as shown in Figure 1.9); with time on stream, these O-containing surface species are transformed to aromatic compounds and eventually to typical coke species, i.e., polycyclic aromatics. Their work explained the deactivation kinetics of the catalyst observed in a different way, in which they pointed out the crucial role of O-containing species in deactivating the catalyst during MTH conversion.\textsuperscript{100} Furthermore, Bhan et al. found that the addition of Y$_2$O$_3$ could improve the lifetime of CHA zeolite in 4-fold for the methanol-to-olefins
reaction. They revealed the function of $Y_2O_3$ as to catalytically decompose formaldehyde (an O-containing compound), which can be produced by acid-catalyzed bimolecular dehydrogenation of methanol during the MTH conversion.\textsuperscript{108}

![Diagram]

**Figure 1.9.** Proposed mechanistic pathway for the formation of O-containing coke (a and b). Reaction of furan with olefins to localized aromatics (c).\textsuperscript{100}

### 1.6 Scope of this dissertation

In this dissertation, I will present our study on the influence of different structured zeolites on the mechanism of MTH conversion. In our work, we first adjusted the structures of zeolite from three aspects, the mesoporosity, the acid density and pores with confinement effect, and then investigated their performances on the MTH conversion. With these works, we tried to obtain some insights into the relationship between structure and mechanism. And finally we hope we can offer some constructive guidance or advice on the catalysts design for highly valuable products in MTH conversion.
Chapter 2 will discuss the influence of mesoporosity in Zeolite Beta on its catalytic performance for the conversion of methanol to hydrocarbons. In this work, we systematically compared the catalytic properties between hierarchically porous Beta-MS with conventional microporous Beta-C for MTH conversions. Our results show that the significant intra-crystalline mesoporosity is indeed advantageous for improving the accessibility of acid sites in the catalyst crystals, and thus give rise to a 2.7-fold larger conversion capacity, a 2.0-fold faster conversion rate, and a remarkably longer catalyst lifetime. More importantly, the mesoporosity plays an important role on the mechanism of MTH conversion. Methylbenzenes, which are the intermediates of the aromatic-based cycle in MTH reaction, can easily diffuse out of the zeolite channels in Beta-MS, limiting the propagation of this catalytic cycle, while relatively promoting the olefin-based cycle. As a consequence, Beta-MS gave lower ethylene selectivity but higher selectivity towards C₄ – C₇ aliphatics with respect to Beta-C in a wide range of methanol conversions.

Chapter 3 will focus on the effect of aluminum content on ethylene selectivity in methanol-to-hydrocarbons conversion on ZSM-5. Ethylene selectivity, for DME conversion at 350 °C and 46 – 52% DME iso-conversion on five ZSM-5 samples with similar crystallite sizes (150 – 240 nm) and Si/Al varying between 55 and 1580, increased from 5.7% on the ZSM-5 sample with low aluminum content (Si/Al = 1580) to 16% on the ZSM-5 sample with high aluminum content (Si/Al = 55). The mechanistic basis for this increase in ethylene selectivity with increasing aluminum content is an increase in
the number of interactions between active sites and methylbenzenes before these molecules exit the zeolite crystallite. Finally, a single-value parameter describes the combined effects of aluminum content and crystallite size on ethylene selectivity for MTH conversion on ZSM-5 zeolite.

**Chapter 4** will report the role of the olefins-based catalytic cycle and its influence on propylene selectivity in the methanol to olefins (MTO) reaction over small-pore DDR zeolite. For MTO reaction at 45 – 55% methanol iso-conversion on investigated DDR zeolites, ethylene selectivity decreased monotonically from 36.6 % to 27.8 % at 400 °C and from 46.2 % to 37.9 % at 450 °C, while propylene selectivity increased monotonically from 38.1 % to 48.3 % at 400 °C and from 36.4 % to 41.1 % at 450 °C as Si/Al increased from 22 to 172. In a DDR sample with a shorter diffusion length, the selectivity toward propylene was further increased to 50.6 % at 400 °C and 43.6 % at 450 °C. Results from \(^{12}\text{C}/^{13}\text{C}\) methanol switch experiments and the analysis of retained active species in used catalysts demonstrate that with the preferential propagation of olefins-based catalytic cycle, the selectivity toward propylene is promoted accordingly. The mechanistic basis is that due to the transport restrictions, the higher olefins are confined inside of the DDR catalyst and then subsequently undergo β-scission to produce propylene predominately.

**Chapter 5** will cover the influences of oxygen-containing compounds on coke formation, catalyst deactivation, product selectivity, and the induction period of the MTH conversion. We first detected trace amounts of oxygen-containing compounds in the
coke formed during the MTH reactions over zeolite catalysts. We demonstrated that the presence of such a compound suppresses the conversion of methanol by prior adsorption on the acid sites of the zeolite, where it can be rapidly converted to aromatics and coke species. As such, these O-containing compounds play crucial roles in deactivating the catalyst by site blocking followed by coke formation. In addition, the conversion of O-containing compounds to aromatics can slightly enhance the aromatics cycle of the MTH reaction, leading to higher selectivity for ethylene.
Chapter 2: Investigating the influence of mesoporosity in zeolite Beta on its catalytic performance for the conversion of methanol-to-hydrocarbons¹

2.1 Introduction

Zeolites which are microporous aluminosilicates contain intra-crystalline cavities and regular channels of molecular dimensions. The small pore sizes in zeolites (0.3—1 nm) render unique shape- and size-selectivity in catalytic reactions,³¹-³² but also lead to constraints for molecular diffusions within the zeolite crystals.²⁸ As a result, zeolite-catalyzed reactions are always limited by the slow diffusion. Decreasing the size of zeolite particles could help to reduce the diffusion length, but it is not favorable because of the difficulty to synthesize zeolite particles smaller than 100 nm, and in further, ultrafine catalysts are difficult to handle and then, undesirable for the practical applications.¹⁰⁹-¹¹⁰ An alternative effective method to circumvent the diffusion limitation is to create a great number of mesopores (> 2 nm) across the zeolite crystals.³⁴,¹¹¹-¹¹² Based on this strategy, it is then possible to reduce the diffusion length significantly (even down to few nanometers), because the mesopores can break the microporous zeolitic framework into the small domains. The resulted materials are generally referred as “mesoporous zeolites” or “hierarchical zeolites,” in which mesopores permit fast

¹ Portions of this chapter have been previously published: ACS Catalysis, 2015, 5, 5837-5845. Reproduced with permission of the American Chemical Society.
diffusion and enhanced accessibility for large molecules, at the same time zeolitic micropores can enable catalytic activity and selectivity during reactions.\textsuperscript{33, 113-114}

Conventional methods to prepare hierarchical zeolites are usually based on various post-synthetic processes like steaming,\textsuperscript{103} base (or acid) leaching,\textsuperscript{115-116} and chemical treating.\textsuperscript{117-119} Recently, much more efforts have been involved in the “direct synthesis” through soft-templating ways,\textsuperscript{120-123} which can achieve better mesoporosity, more precise control on pore sizes, and higher zeolite structure integrities compared with the “post-treatment” routes. Hierarchical zeolites fabricated by different methods have also been tested as catalysts for lots of reactions, and typically, they exhibit better catalytic activities (especially when the substrates are bulky molecules),\textsuperscript{124} longer lifetimes,\textsuperscript{107} slower rates of coke formation,\textsuperscript{105} and altered product distributions\textsuperscript{125} compared to the conventional zeolites having the same frameworks. For example, recently, we reported that a non-surfactant cationic polymer can play as a dual-template to synthesize hierarchical Beta zeolite.\textsuperscript{126} The obtained zeolite (Beta-MS) features remarkable mesoporosity, excellent stability, single crystallinity, and superior catalytic activity than conventional Beta zeolite in many liquid-phase reactions. Although there are many evidences for the superior properties of the hierarchical zeolites, a systematic comparison between hierarchical zeolite and the bulk counterpart for a particular reaction on the basis of detailed catalyst characterization and a careful analysis of the full products is still lacking.
The conversion of MTH has attracted much attention in the past few decades due to it provides an alternative way to produce fuels and chemicals which are mainly produced through petroleum-based routes currently. Acidic zeolite is most commonly used catalyst for MTH reaction.\textsuperscript{15} It is generally known that MTH conversion on zeolite follows an “hydrocarbon pool” mechanism,\textsuperscript{53,127} where the active intermediates repeatedly undergo methylation and cracking reactions to produce the complex hydrocarbons, and that two catalytic cycles are coexisted in this process: an olefin-based cycle and an aromatic-based cycle, in which olefins and polymethylbenzenes act as active hydrocarbon species, respectively (Scheme 2.1).\textsuperscript{17,56-57} This dual-cycle mechanism could help to explain the observed product distribution in MTH conversion on different zeolites by learning how pore structures of zeolite catalysts affect the relative propagation of the two catalytic cycles.\textsuperscript{15} For example, ZSM-22 with one-dimensional non-interacting 10-member-ring channels is too small to form large polymethylbenzene intermediates, and consequently, the aromatic-based cycle is suppressed while the olefin-based cycle dominates the reaction process, leading to high selectivity toward branched C\textsubscript{5+} alkenes.\textsuperscript{58-59} In sharp contrast, SAPO-34 has large 12-member-ring cavities but small (3.8 × 3.8 Å) pore openings which enriches aromatic intermediates, give rise to the promotion on the aromatic-based cycle for more ethylene\textsuperscript{128} (a typical product from this cycle, shown in Scheme 2.1). Likewise, the MTH product distribution on ZSM-5 zeolites can be adjusted by changing the reaction conditions (such as feed compositions\textsuperscript{65,87,129} and crystal sizes\textsuperscript{60,109,130}) to tune the relative propagation of these two cycles.
Scheme 2.1. The proposed dual-cycle mechanism for methanol-to-hydrocarbon conversions over zeolite catalysts. The major intermediate species of the aromatic-based cycle (methylbenzenes) may differ in different zeolites due to pore size differences.

Hierarchical zeolites used for MTH conversion are mainly based on ZSM-5 system. Schmidt et al.\textsuperscript{96} prepared a hierarchical ZSM-5 zeolite via desilication reassembly technique for MTH reaction. They found that besides a longer lifetime, hierarchical ZSM-5 shows a remarkably different deactivation/reactivation behavior from that of conventional ZSM-5. During the successive deactivation/reactivation cycles, conventional ZSM-5 shows a near constant reaction rate but an increasing deactivation rate, while hierarchical ZSM-5 shows the opposite behaviors (a decreasing reaction rate but a constant deactivation rate). Aramburo et al.\textsuperscript{103} found that mesoporous ZSM-5 synthesized through steaming treatment exhibits similar activity and product selectivity but better stability during MTH conversion than that on untreated ZSM-5, and that different coke species are formed in these two catalysts. Ryoo et al.\textsuperscript{131} prepared ZSM-5 nanosheets with only one-unit-cell thickness which exhibits a 5-fold longer lifetime than
the conventional ZSM-5 when compared in MTH conversion. More recently, Bhan’s group\textsuperscript{60} systematically investigated the effect of crystallite size of ZSM-5 on product distribution in MTH reaction. Their results showed that larger crystallite sizes favor the aromatic-based cycle to higher light-olefin selectivity, due to the prolonged intra-crystalline residual time of large methylbenzenes. In this study, hierarchically structured ZSM-5, with a short diffusion length about ~ 1 nm, was used as the representatively smallest crystallite.

In this chapter, we endeavor to explore the influence of mesoporosity in Beta zeolite on its catalytic performance for the MTH conversion by systematically comparing mesoporous Beta zeolite (Beta-MS) with conventional Beta zeolite (Beta-C). We analyzed the full products and further probed the coke species and their distributions in the catalysts by the assistance of electron microscopy and electron energy loss spectroscopy. The data we gained explains the large difference between these two catalysts and then provides important insights on the effect of intra-crystalline mesoporosity of zeolites on their catalytic properties.

\section*{2.2 Experimental section}

\subsection*{2.2.1 Preparation of the catalysts}

Beta-MS was synthesized hydrothermally from an aluminosilicate gel using a cationic polymer (polydiallyldimethylammonium chloride) as the template; the details of its synthesis can be found in the recent publication\textsuperscript{26} 

Beta-C was synthesized based on a
reported method.\textsuperscript{132} To transform zeolites to the H-form, the as-gained zeolites were overnight ion-exchanged with 0.5 M NH$_4$NO$_3$ solution (20 mL per gram of zeolite) for three times, and dried in air at 70°C, and finally calcined at 550°C in air for 4 h.

2.2.2 Characterizations of the catalysts

Scanning transmission electron microscopy (STEM) images were acquired on a FEI Titan ST Microscope operated at 300 KV using a high-angle annular dark field (HAADF) detector. High-resolution TEM was performed on a JEOL JEM-3010 TEM at 300 KV. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was conducted on a Varian 720-ES spectrometer, and the powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer using Cu Kα radiation. Ar adsorption-desorption isotherms were measured on a Micromeritics ASAP 2420 apparatus at 87 K. Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209 F1 machine with the temperature increased from 150 °C to 850 °C under 25 mL/min flowing air and a constant ramping rate of 10 °C/min. NH$_3$ temperature-programmed desorption (TPD) measurements were performed on a Micromeritics AutoChem II 2950 equipment. Before the measurements, 0.15 g sample was pretreated in 25 ml/min He gas for 1 h at 500 °C and then cooled to 100°C. Then, the sample was exposed to a 20 mL/min mixed gas flow (10 mol% NH$_3$ and 90 mol% He) for 1 h to ensure the sufficient adsorption of NH$_3$. Prior to the process of desorption, the sample was flushed by He gas for 3 h. Subsequently, NH$_3$ desorption was performed in the range of 100 – 600°C at a heating rate of 10 °C/min under a 20 mL/min He flow. \textit{In situ} Fourier transform infrared
spectroscopy (FTIR) spectra of pyridine adsorbed were recorded on a Nicolet iS10 FTIR spectrometer, operating in transmission mode. The samples were pre-treated at 450°C in a vacuum for 8 h before adsorbing pyridine at room temperature. Before collecting the spectrum, desorption of pyridine was performed at the desired temperatures for 2 hours. Magic-angle spinning (MAS) $^{27}$Al single-pulse nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance 900 WB NMR spectrometer operated at a magnetic field of 21.1 T. The hydrated samples were packed into a 3.2 mm ZrO$_2$ rotor. Spectra were recorded at a resonance frequency of 234.56 MHz, a spinning rate of 20 KHz, a pulse length of 2.0 μs, and a recycle delay of 1 s for 5000 scans. The chemical shift is referred to an external standard of Al(Cl)$_3$·6H$_2$O ($\delta = 0$ ppm).

2.2.3 Catalytic reactions

MTH reaction was performed in a stainless steel fixed-bed reactor (i.d. 11 mm) packed with 0.5 g zeolite catalyst. Prior to each run, the catalyst bed was activated in a 50 mL/min pure air flow at 550°C for 60 min, after that the temperature was decreased to 330°C, and the air flow was switched to 50 mL/min N$_2$ gas flow mixed with 0.01 mL/min methanol by a HPLC pump. The desired methanol conversions were achieved by tuning the weight hourly space velocity (WHSV) in the range of 0.94 g$_{\text{MeOH}}$ g$_{\text{Cat}}^{-1}$ h$^{-1}$ to 12 g$_{\text{MeOH}}$ g$_{\text{Cat}}^{-1}$ h$^{-1}$. The reactions were all performed under atmospheric pressure, and the product was analyzed by an online gas chromatography. Composition of the effluent was determined by gas chromatography (GC) with a flame ionization detector (FID) equipped
with Agilent HP-PLOT/Q column (30 m*0.53 mm*40 μm). For calculation, dimethyl ether was not considered as a product.

2.2.4 Analysis of residual organic species in used catalysts

Residual soluble organic species retained in catalysts were extracted following a generally used procedure. Specifically, the catalyst was first taken out of the reactor after the desired reaction time, and 200 mg used catalyst was transferred to a capped Teflon vial and dissolved in 6 mL of 24% HF for 3 h. After that, 6.0 mL CH₂Cl₂ was added to the solution in order to extract the organic species from water phase. After 3 h, the organic phase was separated from the mixture, and analyzed in GC and GC–MS equipped with HP-5 column (30 m*0.32 mm*0.25 μm).

The focused ion beam (FIB) technique was used to cut a thin slice from a deactivated catalyst particle for the carbon mapping and electron energy loss spectroscopy (EELS). FIB sample preparation was conducted on an FEI Helios NanoLab 400S FIB/SEM dual-beam system. Before cross sectioning by FIB and the ion milling process, crystal was pre-sputtered by a thin gold layer with a thickness of 5 ~ 10 nm. This layer played as both a marker and a separator between the coke species inside the crystal, and the Pt/C layer outside the catalyst crystal deposited prior to FIB cross sectioning served to protect the sample from being damaged by the ion beam. This step is essential to identify the intrinsic distribution of coke species throughout the cross-section specimen of zeolite and to avoid surface damage by the ion beam and the diffusion of deposited carbonaceous species into the specimen. STEM imaging and EELS were performed on a
cubed Titan G2 electron microscope with a probe-corrector operated at 300 kV. A Cs-corrected and monochromated STEM probe was used for site-specific characterization of the coke species in zeolites as it offers both high-spatial (< 1.4 Å) and high-energy resolution (~ 0.2 eV).

### 2.3 Results and discussion

#### 2.3.1 Characterization of Beta zeolites

These two catalysts investigated in this chapter, hierarchically structured mesoporous Beta zeolite (denoted as Beta-MS) and conventional Beta zeolite (denoted as Beta-C), both have comparable particle sizes (300-500 nm and 400-600 nm for Beta-MS and Beta-C, respectively) and are phase pure, as shown by the STEM and XRD patterns (Figures 2.1a-c). XRD figure shows that the peaks of Beta-MS are slightly little broadened relative to that of Beta-C, which suggests smaller crystallite size of the former zeolite (Figure 2.1c). The HR-STEM images clearly indicate that unlike Beta-C, which consists of dense crystals, Beta-MS crystals have hierarchical structures and a remarkable intra-crystal mesoporosity (insets in Figures 2.1a and b and Figure 2.2). The big difference is then confirmed by Ar adsorption isotherms tested under 87 K. Beta-C exhibits a special type-I isotherm feature of microporous zeolite, however, Beta-MS shows an isotherm combined type-I and type-IV isotherm characteristics, which indicate the coexistence of both micropores and mesopores (Figure 2.1d). Beta-MS shows a slightly larger BET surface area (686 m²/g vs. 623 m²/g) and a remarkably higher total
pore volume (0.84 cm$^3$g$^{-1}$ vs. 0.27 cm$^3$g$^{-1}$) than that of Beta-C. The mesopores of Beta-MS have a relatively narrow size distribution centered at $\sim$8.5 nm, as tested by BJH (Barrett-Joyner-Halenda) model on the adsorption isotherm. HR-TEM images of Beta-MS also show the disordered mesopores breaking the microporous zeolite frameworks into many very small but still continuous domains, where the thickness of the smallest crystalline domain is about 3-nm (Figure 2.2). This data means that Beta-MS zeolite has a short diffusion length of a few nanometers only, which is about two orders of magnitude shorter than that of the counterpart Beta-C. More detailed structural characterizations of Beta-MS, including the single crystalline nature and three-dimensional interconnection of mesopores, can also be found in the recent publication.\textsuperscript{126} Although the same Si/Al ratio (21) was used in the synthetic precursors, the as-gained Beta-MS and Beta-C have slightly different Si/Al ratios (18 and 15, respectively), as determined by the ICP-OES method. Pyridine adsorption/desorption experiments monitored by FTIR spectra revealed a nearly identical Brønsted acidity in these two kinds of catalysts (Figure 2.3). The results gained from the $\text{NH}_3$-TPD experiments show that Beta-MS sample has slightly fewer acid sites compared to that of Beta-C (Figure 2.3b), which is possibly because of its lower Al content, as monitored by the ICP-OES measurement.
Figure 2.1. STEM images of (a) Beta-MS and (b) Beta-C. (c) XRD patterns of Beta-MS and Beta-C. (d) Ar adsorption-desorption isotherms of Beta-MS and Beta-C collected at 87K. The insets in (a) and (b) are enlarged STEM images for individual crystals.
Figure 2.2. HRTEM image of Beta-MS, showing the coexistence of ordered zeolitic microporous channels and disordered mesopores.

Figure 2.3. FTIR spectra of the characteristic ring vibrations of pyridine adsorbed on Brönsted (B) and Lewis (L) acid sites over Beta-MS (a) and Beta-C (b) catalysts upon desorption treatment at different temperatures. (c) NH$_3$-TPD profiles of Beta-MS and Beta-C.

The locations of tetrahedrally coordinated Al sites (Al T-sites) in zeolite lattices usually determine their stability and accessibility and always impact their acidity of the zeolites.$^{134-136}$ It is very important and interesting to explore whether the formation of a
hierarchical structure (i.e., the incorporation of mesopores) can cause the Al T-site distribution to differ for a given zeolite topology. Very recently, Vjunov et al. used the ultrahigh-field $^{27}$Al MAS NMR to probe the distribution of Al sites among the nine crystallographically distinct T-sites in zeolite Beta (T1-T9 sites, see Figure 2.4), and their analysis was also based on the deconvolution of spectra according to a DFT-predicted $^{27}$Al NMR chemical shifts. Based on this already established method, here then, we probed the Al distribution in these two samples, Beta-MS and Beta-C. Figure 2.5 shows the result on $^{27}$Al NMR spectra monitored at 900 MHz, in which by fitting the experimental spectra based on the DFT-calculated $^{27}$Al NMR chemical shifts, and the relative occupancies of Al element at different T-sites were then determined. The results clearly show that Al element was preferentially occupied in T2 site and disfavored the T4, T5, T6, and T8 sites in both samples Beta-C and Beta-MS. The main difference between these two samples appears in the fraction of T7 site, which is considerably higher in Beta-MS (0.25) than that in Beta-C (0.09). T7 site is part of 5- and 6-member rings but unassociated with 4-member rings. The observed distribution of Al element depends on the occupation probability of Al at each T site as well as the quantity of each T site in the zeolite framework. If assuming that the occupation probabilities are equal for both Beta-MS and Beta-C, we could conclude that the formation of mesopores (with our direct-synthesis path) leads to a great number of the surface terminations, and thus, a change on the relative quantities of different T-sites happens in Beta zeolite. These data indicate that although showing a same framework topology, these two samples (Beta-MS and Beta-C) are substantially different in the
distribution of Al T-sites. Exploring the slight effects of this difference on the acid strength of the catalyst is beyond the scope of our study, in which we assume that the different catalytic behaviors between hierarchical zeolite and conventional zeolite are mainly associated to the transport properties.

Figure 2.4. Structure model of zeolite Beta with nine crystallographic distinct sites labelled. The Oxygen atoms are not shown for clarity.

2.3.2 Catalytic performance of Beta catalysts

Beta-MS and Beta-C for MTH reaction were tested in a fix-bed reactor at 330 °C and 101 KPa total feed pressure. We adjusted the initial conversion of methanol by varying the reaction WHSV. Product analysis was then performed at steady-state conversions. The details of reaction conditions and product analysis methods are elaborated in 2.2 experimental section.
Figure 2.5. MAS $^{27}$Al single-pulse NMR spectra of Beta-MS (a) and Beta-C (b) with the according distribution of different T sites on the right-hand side. The chemical shifts of different T sites by DFT calculations used for fitting were adopted from reference. The fitting procedure was similar to that described in the related reference. The black dots and red curves represent the experimental and fitted spectra, respectively. See Figure 2.4 for the nine crystallographic T sites in the zeolite BEA framework.

At first, the intrinsic selectivity for each catalyst at low conversions was investigated. In order to achieve an iso-conversion of methanol, a much larger WHSV was needed for Beta-MS because of its higher activity than Beta-C. Specifically, Beta-MS and Beta-C gave around 20% conversion of methanol (at 30 min time-on-stream) at the WHSV of 12 g$_{\text{MeOH}}$ g$_{\text{Cat}}^{-1}$ h$^{-1}$ and 5 g$_{\text{MeOH}}$ g$_{\text{Cat}}^{-1}$ h$^{-1}$, respectively. Figure 2.6a shows the product
selectivity toward ethylene, propylene, C_4-C_7 aliphatics, methylbenzenes (MBs), and “others” including ethane, propane, and C_8+ hydrocarbons excluding MBs. It is generally documented that ethylene is a terminal product from the aromatics-based catalytic cycle in MTH reaction. Therefore, ethylene selectivity can thus be used as an indicator for the degree of propagation of this aromatics-based cycle.\textsuperscript{17, 65, 129} Likewise, higher-aliphatics (e.g., C_4-C_7) selectivity is always used to reflect the propagation of the olefin-based catalytic cycle (Scheme 2.1).\textsuperscript{17, 65, 129} Being noted that because propylene can be produced from both catalytic cycles, and aromatics act as the intermediates of aromatic-based cycle, their selectivities are therefore not suitable to describe the propagation of these two cycles. And thus, we use the ratio of ethylene to C_4-C_7 (ethylene/C_4-C_7) as a “descriptor” for the relative propagation of these two catalytic cycles. As shown in Figure 2.6a, Beta-MS produced less ethylene but more C_4-C_7 aliphatics than Beta-C, giving a smaller ethylene/C_4-C_7 yield value (0.095 vs. 0.15). Reducing the WHSV to 7 g_{\text{MeOH}} g_{\text{Cat}}^{-1} h^{-1} for Beta-MS and to 3 g_{\text{MeOH}} g_{\text{Cat}}^{-1} h^{-1} for Beta-C led to a methanol conversion increasing to \textasciitilde55%, while Beta-MS still showed a lower ethylene selectivity, a higher C_4-C_7 selectivity, and accordingly a smaller ethylene/C_4-C_7 yield (0.11 vs. 0.16) than did Beta-C (Figure 2.6b). These data suggest that mesopores incorporated in Beta zeolite favors the olefin-based catalytic cycle over the aromatics-based catalytic cycle in MTH reaction. At an earlier time of 2015, Bhan’s group found that ethylene selectivity decreased while C_4-C_7 hydrocarbons selectivity increased with the decrease of crystallite size of ZSM-5 catalysts. They claimed that the aromatics-based cycle is suppressed by the short diffusion lengths because of that the formed
bulky methylbenzene intermediates can easily exit from micropores without undergoing further dealkylation reactions that are integral for the aromatics-based cycle which produces ethylene. Because our data are in a good agreement with their observations, we can thus infer that although the 12-member-ring channels of zeolite Beta are sufficiently large for most molecules involved in MTH conversion without diffusion restriction, the creation of intra-crystalline mesoporosity imposes a similar effect on the product distribution as has been found for ZSM-5. We noted that the effect of crystallite size on the product selectivity is more significant for ZSM-5 than for Beta, most likely because ZSM-5 has narrower pores (more severe diffusion restriction).

Figure 2.6. Product selectivity over Beta-MS and Beta-C at two iso-conversion (of methanol) conditions: (a) ~20% and (b) ~55%. C₂+, C₃+, C₄-C₇, and MBs stand for ethylene, propylene, C₄-C₇ aliphatics, and methylbenzenes, respectively. The percentages in the horizontal axis specify the exact conversion values given by the corresponding catalyst.
The catalytic performances of Beta-MS and Beta-C were also evaluated in terms of conversion capacity, selectivity, reaction/deactivation rate, and lifetime at high conversions of methanol. For this purpose, we then adjusted the WHSV to be $0.94 \frac{g_{\text{MeOH}}}{g_{\text{Cat}} \cdot h}$ for both catalysts to make sure that they handled same quality of feedstock. Under this conditions, Beta-MS and Beta-C gave 100% and 97% conversions, respectively, at the initial time of the MTH reaction. With a prolonged time-on-stream, conversions of methanol gradually decreased due to the deactivation of catalysts. Notably, Beta-MS exhibited a remarkably slower deactivation rate than that of Beta-C. As shown by Figure 2.7, the lifetime till the conversion of methanol dropped to 50% was 24.5 h for Beta-MS and 9.0 h for Beta-C, respectively.

![Catalytic lifetime in MTH reactions over Beta-MS and Beta-C catalysts at 330 °C and a WHSV of 0.94 $\frac{g_{\text{MeOH}}}{g_{\text{Cat}} \cdot h}$](image)

**Figure 2.7.** Catalytic lifetime in MTH reactions over Beta-MS and Beta-C catalysts at 330 °C and a WHSV of 0.94 $\frac{g_{\text{MeOH}}}{g_{\text{Cat}} \cdot h}$. 
Table 2.1. Factors of catalytic performance derived from Janssens’ model

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>t_{0.5}</th>
<th>t_{0.8}</th>
<th>R</th>
<th>k</th>
<th>a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(h)^b</td>
<td>(h)^c</td>
<td>(mol_{MeOH} g_{Cat}^{-1})^d</td>
<td>(mol_{MeOH} g_{Cat}^{-1} h^{-1})^e</td>
<td>(g_{Cat} mol_{MeOH}^{-1})^f</td>
</tr>
<tr>
<td>Beta-C</td>
<td>9</td>
<td>2.5</td>
<td>0.27</td>
<td>0.6</td>
<td>0.378</td>
</tr>
<tr>
<td>Beta-MS</td>
<td>24.5</td>
<td>16</td>
<td>0.72</td>
<td>1.2</td>
<td>0.139</td>
</tr>
</tbody>
</table>

^a^ refer to reference 140 for the details of this model; ^b^ time until 50% of conversion;
^c^ time until 80% of conversion; ^d^ methanol conversion capacity calculated at t_{0.5}: \( R = WHSV_{MeOH} * t_{0.5} \);
^e^ rate constant k derived from Janssens’ model at t_{0.8}.
^f^ deactivation coefficient: \( a = t_0 / t_{0.5} \) (contact time: \( t_0 = 3.4 \ g_{Cat} \ h \ mol_{MeOH}^{-1} \)).

Here, a model proposed by Janssens was used to calculate the conversion capacity \( R \), the rate constant \( k \), and the deactivation coefficient \( a \) from the lifetime plots of both catalysts.\(^{139}\) Clearly, the results show that Beta-MS gives a greater conversion capacity \( R \) (0.72 vs. 0.27 mol_{MeOH} g_{Cat}^{-1}), a higher rate constant \( k \) (1.2 vs. 0.6 mol_{MeOH} g_{Cat}^{-1} h^{-1}), and a lower deactivation coefficient \( a \) (0.139 vs. 0.378 g_{Cat} mol_{MeOH}^{-1}) than that of Beta-C (Table 2.1). Given that these two catalysts both have an identical topology type with comparable crystal sizes and Si/Al ratios, the superior catalytic performance from Beta-MS can thus be attributed to the unique hierarchical structure. The highly interconnected mesoporous network inside of Beta-MS crystals allows all acid sites in the catalyst crystals to be totally accessible, and thus, leads to a higher conversion rate.
and a larger conversion capacity; at the same time, it reduces the probability of coke formation (by promoting molecular transport of bulky ones) and increases the coke tolerance capacity, which accounts for the longer lifetime. In sharp contrast, because of the diffusion restrictions, the methanol conversion over Beta-C zeolite mainly takes place on the outer layer of catalyst crystals in which the formed coke species are easily accumulated, thus blocking the reacting molecule access to the interior acid sites and therefore quickly deactivating the catalyst. The insufficient usage of the active sites can explain the inferior catalytic performance of Beta-C zeolite compared to Beta-MS zeolite. We also verified the hypotheses by testing the coke distribution in the fully deactivated catalysts (*vide infra*).

We then analyzed the changes of product distribution with time-on-stream until these catalysts were both essentially deactivated (conversion < 20%). As illustrated in Figure 2.8, Beta-MS and Beta-C show similar evolution trends of the product distribution. At the initial time of the MTH reaction, both catalysts gave C₄-C₇ aliphatics as the main products (butylene dominating in this fraction), but their selectivity were quickly decreased with the reaction proceeded. Propane was the other product with a decreased selectivity, while all other identified products, including aromatics, methane, ethylene, and propylene, showed gradually increased or constant selectivity with prolonged time-on-stream (*Figure 2.8a and b*). These data show that over both Beta catalysts, the olefin-based catalytic cycle dominates at the initial time of the MTH reaction, but the aromatic-based catalytic cycle is gradually boosted with the reaction
proceeding. Meanwhile, many certain obvious differences over selectivity were evident between these two catalysts. Beta-MS produced more C₄-C₇ aliphatics than Beta-C throughout all the lifetime: selectivity decreased from 61% to 38% over 30 h for Beta-MS but from 46% to 31% within 12 h for Beta-C (Figure 2.8c). Butylene is the main part of C₄-C₇ aliphatics in both catalysts, when we compared these two catalysts, there was more butylene produced from Beta-MS than Beta-C throughout all the lifetime. The selectivity toward butylene in Beta-MS could reach to 46% at the very beginning and decreased to 18% at the end of its lifetime. While, there was 35% of butylene in Beta-C at the initial time, which dropped to 15% at the end. Alternatively, over the whole reaction period, zeolite Beta-MS had lower ethylene selectivity and methane selectivity than Beta-C (Figure 2.8c). As mentioned, because ethylene and methane are both terminal products from the aromatic-based cycle via the process of dealkylation of MBs,¹⁷, ⁶⁵, ¹²⁹ we can thus conclude that Beta-MS zeolite favors the olefin-based cycle over the aromatic-based cycle, compared to Beta-C. These data are consistent with the results discussed above regarding the low methanol conversions, and can therefore be attributed to the feasible molecular transport from the Beta-MS which reduces the opportunities for methylbenzenes to undergo the process of multiple methylation/dealkylation reactions.
Figure 2.8. Evolution of product distribution during the MTH conversion reaction over (a) Beta-MS and (b) Beta-C. In (c), the selectivities towards C₄-C₇ aliphatics, ethylene, and methane shown in (a) and (b) are isolated for direct comparison between the two catalysts.

2.3.3 Analysis of coke species in the spent catalysts

Next, we then investigated the coke species formed in both catalysts to help a further explain on their different catalytic behaviors. Thermogravimetric analysis (TGA) of the spent catalyst measured the coke amount based on the weight loss between the temperature of 300 and 800 °C. Interestingly, we found that despite converting much more methanol (Figure 2.7), Beta-MS produced much less coke than that of Beta-C at same reaction time; such as, after 5 h, the coke contents were tested for Beta-MS and Beta-C at 8.7 wt% and 11.7 wt%, respectively (Figure 2.9a). The slower coke formation from Beta-MS can be attributed to the hierarchical structure, which can provide better
molecular diffusion to suppress the polymerization of the aromatics. However, when totally deactivated, much more coke was accumulated in Beta-MS (16.8 wt%) than that in Beta-C (13.5 wt%), showing that Beta-MS zeolite has a much higher tolerance capacity to coke (Figure 2.9b). We then used FIB technique to cut ultrathin cross-section specimens (60 ~ 80-nm thick) out of completely deactivated catalyst particles. From the specimens, we can probe the distribution of the coke species in these two catalysts by STEM and EELS. The elemental carbon (K-edge) mapping from EELS reveals a marked difference between these two catalysts: Beta-MS exhibits a uniform coke distribution throughout the whole crystal, while Beta-C shows an inhomogeneous coke distribution which is concentrated at the outer layer and scarce in the inner region of the particle (Figure 2.10). This data is in good agreement with the TGA test which shows that zeolite Beta-MS can tolerate much more coke than zeolite Beta-C. More importantly, it also reveals the different reaction sites in these two catalysts. With Beta-C, because of the diffusion restriction imposed by microporous network, the conversion essentially happens at the outer surface of the catalyst crystals, in which once a dense coke layer is formed, the interior acid sites are blocked and thus become useless to catalytic reaction. As to Beta-MS, all acid sites in the catalyst are accessible due to the hierarchical structure that circumvents the diffusion constraint. This difference illustrates the reason on the greater conversion capacity, the faster reaction rate, and longer lifetime of Beta-MS catalyst compared to that of Beta-C catalyst.
Figure 2.9. (a) TGA analysis of Beta-MS and Beta-C catalysts after 5 h of reaction. (b) TGA analysis of the completely deactivated Beta-MS and Beta-C catalysts. The weight losses indicated in the figure correspond to the coke contents.

Figure 2.10. Spectra images including HAADF-STEM images (left), carbon K-edge intensity maps (middle), and line profiles (right) of Beta-MS (a-c) and Beta-C (d-f). Yellow contour lines in (b) and (e) mark the Au-layers, which show sharp bright contrast in (a) and (d). The intensity maps in (b) and (e) were rendered using a temperature color scheme as indicated by the color bar. Red arrows indicate where the line profiles were extracted.
In addition to the overall coke distribution, high-resolution EELS (energy resolution of about 0.2 eV along with a small focal depth of less than 10 nm) allowed us to probe the chemical nature of the coke species deposited at specific locations of the catalyst particles. From another two FIB-cut specimen (two specimen used for Figure 2.10 were contaminated with the scanning of carbon mapping), we then acquired two EELS spectra of Beta-MS by focusing the electron beam on a mesoporous region (site 1) and a zeolite domain (site 2), respectively, and one EELS spectra of Beta-C (site 3) (as seen in Figure 2.11). By comparing the EELS fine structures of these three sites, we found that site 1 had a 1s→π* excitation at 285.1 eV, which is previously assigned to the species of large aromatics in high degrees of graphitization\cite{140,141} but didn’t appear in the spectra of sites 2 or 3 (Figure 2.11). Sites 2 and 3 both showed a peak of energy loss (288.6 eV for site 2 and 288.4 eV for site 3) that is absent from site 1. These peaks can be assigned to the C-H 1s-3p/σ* resonance, and thus considered to be indicator of H-rich hydrocarbon species, reasonably.\cite{141} These data suggest that for conventional Beta zeolites, the coke resided in the micropores are H-rich deposits with low molecular weight (e.g., MBs and long-chain aliphatics), while the heavier graphite-like coke species are deposited only on the outer surface of the catalyst crystals. This is conceivable to consider the small dimensions of zeolite micropores. As to the Beta-MS, however, the space of intra-crystalline mesopores is sufficiently large for the accommodation of heavy coke species with high degree of graphitization. More importantly, we found another 1s→π* excitation at ~286.5 eV in the spectra for both zeolite Beta-MS and zeolite Beta-C (Figure 2.11), which is generally a sign of the existence of aromatic C=O sp² carbon
species.\textsuperscript{141} It was previously proposed that the oxygen-containing species may be a possible reason for the deactivation of the catalysts, especially at the initial thime of the reaction.\textsuperscript{100} However, no specific O-containing compounds have been identified yet, and the formation mechanism still remains unclear. These EELS results provide further evidence for the existence of O-containing species and specifies that they contain aromatic C=O bonds.

\textbf{Figure 2.11.} HAADF-STEM images of cross sections of Beta-MS (a) and Beta-C (b). Local regions are enlarged to show the locations of EELS spectra (on the right) collected. An irregular mesopore in Beta-MS is outlined in yellow in the zoomed image. Carbon K-edge EELS spectra collected in sites 1, 2, and 3 are shown on right, where different characteristic energy loss peaks are marked by dashed lines with different colors (red: \(~285.1\) eV; blue: \(~286.5\) eV and green: \(~288.4\) eV).

In order to gain more information on the coke, the organic species retained in catalysts were extracted after certain different reaction times by the standard method, dissolution of zeolite aluminosilicate framework in HF solution followed by the process of extraction of organic species by \(\text{CH}_2\text{Cl}_2\) from water phase.\textsuperscript{101-102, 133} These soluble species, essentially the H-rich hydrocarbons residing in catalysts and accounting for \(~5\) wt\% of the total coke amount, were finally analyzed in GC and GC–MS. In agreement to
the EELS result, an O-containing compound (4-methyl-benzaldehyde, C₆H₈O) was identified at the retention time of 25 min (see Figure 2.12) and MS (m/z=120). This compound was detected in both Beta-MS and Beta-C catalysts at different reaction times (Figure 2.12). It is also worth noting that we identified two other oxo-hydrocarbons (di- and tri-methyl-2-Cyclopenten-1-one) in the coke when ZSM-5 was used for MTH reaction. A detailed analysis of these coke species, including the content, formation mechanism, and influences on the catalyst activity, will be talked in Chapter 5.

Figure 2.12. Residual hydrocarbon species extracted from the used catalysts after different reaction times (5h, 10h, and 15 h for Beta-C; 5h, 15 h, and 34 h for Beta-MS).
With the exception of O-containing compounds, we classified the soluble organic species into MBs (dominated by hexamethylbenzene and pentamethylbenzene) and long-chain aliphatics \((C_{10}, C_{11}, C_{12}, C_{14}, \text{etc.})\). As illustrated in Figure 2.12, the relative proportions of long-chain aliphatics and MBs differ greatly between zeolite Beta-MS and zeolite Beta-C. With increasing the reaction time from 5 h to 15 h, the relative content of MBs in Beta-C catalyst gradually accumulated. In a comparison, an obviously smaller fraction of MBs remained in zeolite Beta-MS, even when the catalyst was completely deactivated (at 34 h of reaction). On the other hand, there was a larger fraction of long-chain aliphatics remained in Beta-MS than that in Beta-C regardless of the reaction times (Figure 2.12). These data provide further evidence for the aforementioned proposal that Beta-MS catalyst allows for the fast diffusion of bulky MBs out of the channels because of the hierarchical structure, therefore suppressing the propagation of the aromatic-based cycle relative to the olefin-based cycle; the opposite effect applies to Beta-C catalyst.

### 2.4 Conclusions

In summary, we systematically compared the catalytic properties between hierarchically porous Beta-MS with conventional microporous Beta-C for MTH conversions in this chapter. Our results clearly show that the significant intra-crystalline mesoporosity is indeed advantageous for improving the accessibility of acid sites in the catalyst crystals, and thus leads to a larger conversion capacity, a faster conversion rate, and a longer catalyst lifetime. It also enables Beta-MS catalyst to afford more coke than Beta-C...
catalyst before the complete deactivation. On the other hand, two orders of magnitude difference in diffusion length results in different product distribution between Beta-MS zeolite and Beta-C zeolite. Methylbenzenes, the intermediates of aromatic-based catalytic cycle in MTH reaction, can easily diffuse out from the zeolite channels of Beta-MS, which limits the propagation of this catalytic cycle, while relatively promotes the olefin-based cycle. As a result, Beta-MS gave lower ethylene selectivity but higher selectivity to C₄-C₇ aliphatics compared to Beta-C in a wide range of methanol conversions (20% to 100%). We analyzed the residual coke species in the spent catalysts and found a smaller ratio of MBs: long-chain aliphatics in Beta-MS catalyst with respect to Beta-C catalyst regardless of the reaction time. This data provides further evidence for the suppressed aromatic-based cycle in Beta-MS. Via FIB, STEM, and EELS techniques, we were able to visualize the coke distribution in the spent catalysts. The results verify our hypothesis that all the acid sites in Beta-MS were fully used for catalysis whereas a large fraction of acid sites in Beta-C was blocked (useless for catalysis) by a layer of coke deposited on the crystal’s outer surfaces. Results from EELS implied the presence of oxygen-containing compounds in the coke. The formation mechanism of such a compound in MTH reactions has little exposure in the literature and its role in deactivating the catalyst may be worthy of careful investigations.
Chapter 3: The effect of aluminum content on ethylene selectivity during methanol-to-hydrocarbons conversion on ZSM-5²

3.1 Introduction

The conversion of methanol or dimethyl ether (DME, the dehydration product), proceeds an autocatalytic route with aromatics- and olefins-based intermediates, which constitute the so-called hydrocarbon pools, acting as the organic co-catalysts in the formation of carbon-carbon bond¹⁵, ¹⁴²-¹⁴³. The complicated network of MTH reaction over the microporous acidic zeolite catalysts is now summarized by the dual-catalytic cycles in which the aromatics-based chemistries of methylation and dealkylation are coupled with olefins-based chemistries of methylation and β-scission by hydrogen transfer and cyclization events¹⁷, ⁶⁵. The product distributions in MTH reaction over MFI framework zeolites is recognized to be sensitive to reaction temperatures⁸⁹-⁹¹, textural properties⁶⁵, ⁵⁵-⁵⁶, and feedstock identities⁶⁵, ⁸⁷-⁸⁸. Generally, these effects from the catalyst compositions and morphologies and from process conditions can thus be mechanistically rationalized as a result of the relative extents on the propagation of the aromatics- and the olefins-based cycles¹⁷.

Previously, the isotopic switching experiments done by Svelle and coworkers ⁵⁶-⁵⁷ on ZSM-5 in which ¹²C-methanol feed was switched by ¹³C-methanol feed during the steady

² Portions of this chapter have been previously published: Journal of Catalysis, 2017, 348, 300-305. Reproduced with permission of Elsevier.
state reaction has showed that post-switch the $^{13}$C-content in ethylene closely matched to that of methylbenzenes, while that in higher olefins matched with each other. Ilias and coworkers$^{142}$ showed that ethylene could react $\sim$20 times slower than DME in the reaction of $^{13}$C$_2$-DME ($\sim$ 70 kPa) and 7 – 8 kPa of $^{12}$C$_2$-ethene mixtures on ZSM-5 at 350 °C. In addition, the kinetic measurements by Hill et al.$^{69-71}$ and Svelle et al.$^{144-145}$ showed that the reaction rate of ethylene methylation is at least one order of magnitude slower than that of propene or butylene methylation on ZSM-5 which suggests that ethylene can be considered a terminal product from aromatics-based cycle.

The isotopic switching experiments by Svelle and coworkers$^{56-57}$ also showed that the similar time-evolution of $^{13}$C-incorporation into C$_3$+ olefins suggested that higher olefins (like isobutene and 2-methyl-2-butene) were products from the olefins-based catalytic cycle. The selectivity toward 2-methyl-2-butene and 2-methylbutane in MTH reaction is dependent on the extent of hydrogen transfer, however, it is shown by Aditya’s group that the sum of the yields of 2-methylbutane and 2-methyl-2-butene is largely independent on the chemical conversion$^{64}$ and, that thus the value of ethylene/2-methyl-2-butene varies systematically and predictably with feedstock compositions$^{97}$, reaction temperatures$^{60}$, and crystallite sizes$^{60}$.

Khare et al.$^{143}$ systemically investigated the MTH reaction over a diffusion-free ZSM-5 zeolite at 450 °C and showed that aromatics don’t dealkylate in the absence of methanol or DME once complete DME/methanol conversion is achieved and thus the
dominant chemistry in these reaction conditions is the olefin inter-conversion. A mechanistic basis on the influence of zeolite morphology or composition on MTH selectivity in terms of the dual-cycle hydrocarbon-pool mechanism can thus only be inferred from the results acquired under reaction conditions where both the olefins- and aromatics-based catalytic cycles are active, i.e. under the sub-complete methanol/DME conversion conditions.

In our last chapter, we investigated the influence of mesoporosity in Beta zeolite on the conversion of MTH. In this project, we then studied the effects of another factor (i.e. aluminum content) on ethylene selectivity for MTH conversion. The reactions were carried out at 350 °C over five ZSM-5 samples which had similar crystallite sizes (150 – 240 nm), with an underlying proposal that increasing the intensity of active sites should be able to increase the propagation of aromatics-based catalytic cycle. An increase in aluminum content will increase the number of interactions between the methylbenzenes (which are intermediates of aromatics-based catalytic cycle) and Brønsted acid sites before these aromatics diffuse out from the zeolite crystallite. This increase on the number of the interactions will enable polymethylbenzenes (MBs) to undergo multiple methylation/dealkylation reactions and then produce more light olefins in the process, especially ethylene, and thereby increase its selectivity in the product distribution. And finally, we also propose a single-value descriptor ($N_{\text{H}^+}$), which conflates the effects of crystallite size and aluminum content on ethylene selectivity for MTH conversion over MFI-type zeolites.
3.2 Experimental section

3.2.1. Synthesis of HZSM-5 zeolite samples

Five ZSM-5 samples with similar crystallite size (150 – 240 nm), and Si/Al ratios varying between 55 and 1580 were prepared via the hydrothermal synthesis method based on a previously reported protocol.\textsuperscript{146-147} In a typical synthetic method of a ZSM-5 sample (described for ZSM-5-55), 0.54 g of Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}·16H\textsubscript{2}O (Sigma-Aldrich) was added to 10 mL tetrapropylammonium hydroxide (15 wt\%) aqueous solution (Sigma-Aldrich) with stirring, followed by addition of 6 mL of TEOS (tetraethyl orthosilicate, Sigma-Aldrich). The mixture was then stirred for 6 h and transferred to an autoclave for the process of crystallization at 180 °C for 12 h. The as-synthesized products were recovered by centrifugation, washed several times with H\textsubscript{2}O, and finally dried under air. The as-obtained powders were treated in dry air at 550 °C for 6 h in order to remove the organic structure-directing template. Other ZSM-5 samples with different Si/Al ratios were synthesized by adjusting the amount of Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}·16H\textsubscript{2}O in the synthetic precursors without any other condition changed.

The as-synthesized ZSM-5 samples were then ion-exchanged with NH\textsubscript{4}\textsuperscript{+} ions followed by a treatment in flowing air to convert the NH\textsubscript{4}-exchanged ZSM-5 to the protonated form. In detail, catalyst powder (~ 8 g) was mixed with a 1 M NH\textsubscript{4}NO\textsubscript{3} (Sigma-Aldrich) solution (~ 100 mL) and stirred at 80 °C for 5 h. The powder was then filtered using a Buchner funnel and a 1-micron filter paper and subsequently washed with H\textsubscript{2}O till the pH was around 7. The filtered powders were dried in an oven at 120 °C for 1 h. At last, the ZSM-
5 samples were treated in air (100 mL/min, Minneapolis Oxygen, 20-21% O₂, <10 ppm H₂O) at 550 °C for 4 h. The calcining temperature was increasing from room temperature to 550 °C in 8 h and was held for 4 h. This entire procedure was repeated three times to convert the samples completely to protonated forms. The ZSM-5 samples were then pressed, crushed, and sieved between 40- and 80-mesh sieves to gain uniform particles with size between 180 and 425 µm.

These catalysts are referred to as HZSM-5-X, where X corresponds to Si/Al ratios in the materials as determined by inductively coupled plasma-optical emission spectrometry (ICP-OES).

### 3.2.2. Structural and chemical characterization of ZSM-5 samples

XRD (X-ray diffraction) patterns were recorded on a Bruker D8 Advance diffractometer using Cu-Kα radiation (1.54 Å) for 2θ from 5° to 35°. TEM (Transmission electron microscopy) was performed on a FEI-Tecnai T12 microscope operated at 120 KV. The elemental composition of zeolite samples was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a Thermo Fischer iCap 7000 instrument. The samples were first digested in HF prior to the analysis and diluted 10–100 times to achieve concentrations of Si or Al between 1–10 ppm. NH₃ temperature programmed desorption (TPD) was performed to estimate the concentration of Brønsted acid sites.
Argon adsorption-desorption isotherms were performed on a Micromeritics 3 Flex Surface Characterization Analyzer at 87 K. Prior to the adsorption-desorption measurements, the samples were first degassed at 400 °C for 8 h under high vacuum. The total surface area was calculated using the BET (Brunauer–Emmett–Teller) method, and the surface area of the micropores was estimated by NLDFT method. Total pore volumes of the samples were measured at the absorption pressure $P/P_0 = 0.95$, and the micropore volume (<1.5 nm) was estimated by NLDFT method.

Adsorption uptake measurements of 2,2-dimethylbutane (2,2-dmb) was carried out to estimate the average crystallite size of the as-synthesized ZSM-5 zeolites. The test on the adsorption of 2,2-dimethylbutane was performed on a Micromeritics ASAP 2020 surface area and porosity analyzer which is equipped with a vapor option using the rate of adsorption software. Prior to test, the catalyst sample (~25 mg) was degassed at 450 °C for 4 h under high vacuum. The adsorption data were collected at 25 °C and 13 – 15 kPa 2,2-dimethylbutane pressure. The 2,2-dimethylbutane vapor source was kept at a temperature of 30 °C. (This test was finished in Aditya’s group at University of Minnesota)

For the ammonia temperature programmed desorption (TPD) measurements, ~50 mg samples were loaded in a fixed bed reactor for the test. At first, the samples were pretreated in 100 mL/min dry air at 550 °C for 4 h. The temperature was increased from room temperature to 550 °C in 8 h and was held at 550 °C for 4 h before cooled down to 100 °C. The catalyst was then exposed to ammonia at 100 °C by flowing a mixture of 10
mL/min ammonia and 60 mL/min He. The flow was stopped once the sample was saturated and ammonia uptake was negligible. After saturation, the catalyst was flushed in 60 mL/min He at 100 °C for 8 h in order to remove the physisorbed ammonia. The temperature of the catalyst bed was then increased from 100 °C to 550 °C with a 60 mL/min He, and at the same time the amount of ammonia in the effluent was measured on a Cirrus 2 MKS quadrupole online mass spectrometer (MS) using signal at m/z = 17. The NH₃-TPD measurements could not carried out on HZSM-5-1119 and HZSM-5-1580 samples because of the experimental limitations in assessing these samples with very low Al-content.

3.2.3. Catalytic reactions on a packed-bed reactor

Catalytic reactions of DME were carried out in a 316/316L stainless steel packed-bed reactor (1/4 in OD; 0.035 in wall thickness) equipped with a concentric thermal well (1/16 in OD, 0.014 in wall thickness). Isothermal conditions were maintained in the catalyst bed using a heating coil (ARi Industries Inc., AeroRod® heating assembly) regulated by a Watlow 96 series temperature controller. A K-type thermocouple (Omega Engineering, 0.020 in probe diameter), inserted into the concentric thermal well, was used to measure the temperature of catalyst bed during the reaction. Reactions were performed using 13 – 45 mg catalyst diluted with ~100 mg quartz sand. Quartz sand (Acros Organics) was used as a diluent in the catalyst bed to prevent temperature rise due to the exothermic nature of MTH conversion. Prior to its use, the quartz sand was washed with 1 M nitric acid (Sigma-Aldrich), rinsed several times with deionized
water, dried, and sieved between 40- and 80- mesh sieves to obtain uniformly sized particles. Prior to each reaction, the catalyst was pretreated in 100 mL/min dry air at 550 °C for 4 h. The temperature of the catalyst bed was increased from room temperature to 550 °C in 8 h and was held at 550 °C for 4 h before the sample was cooled down to the reaction temperature. Following the pretreatment, the catalyst was flushed with 100 mL/min He for 1 h.

The reactant stream constituted DME and a mixture of CH₄ and Ar (Airgas, 10% CH₄, 90% Ar) which was used as an internal standard. Gas flow rates were maintained using Brooks Instrument 5850S/SLA5850 series mass flow controllers. The weight hourly space velocity was varied between 0.3 – 2.5 mol C (mol Al-s)⁻¹ in order to achieve the desired chemical iso-conversions (46 – 52%). Methanol was not considered as a product in the calculation of net conversion. The total feed pressure was maintained at 103 – 106 kPa and all of the reactions were carried out at 350 °C. The temperature variation in the bed was less than 1 °C during the reaction. The reactor effluent was analyzed using an online Agilent 7890A series GC (gas chromatograph) – Agilent 5975C series MS (mass spectrometer) equipped with a 100% dimethylpolysiloxane Agilent J&W HP-1 column (50 m × 320 μm × 0.52 μm) connected to a flame ionization detector (FID) and a mass selective detector (MSD), and an Agilent J&W GS-GasPro column (60 m × 320 μm) connected to a thermal conductivity detector (TCD). (This test was finished in Aditya’s group at the University of Minnesota)
3.3 Results and discussion

3.3.1. Structural and chemical characterization

Table 3.1 shows the Si/Al ratios of ZSM-5 samples which were determined from the ICP-OES elemental analysis and the acid site density determined from NH₃-TPD measurements (Figure 3.1). The acid density of each as-synthesized ZSM-5 sample is consistent very well with its Si/Al ratio, showing nearly complete incorporation of Al in the zeolite frameworks of these samples. The XRD patterns of the as-gained ZSM-5 samples are presented in Figure 3.2 and demonstrate that all the as-gained samples are well crystallized with MFI-type topology. Figure 3.3 is the TEM images of the ZSM-5 samples and confirms that all the as-synthesized samples have nearly identical particle-size distributions despite the varied Al content. And the particle sizes calculated based on TEM images are also presented in Table 3.1.

Table 3.1. Si/Al ratios, acid site densities, and particle/crystallite sizes of HZSM-5 samples investigated in this work.

<table>
<thead>
<tr>
<th>Zeolite sample</th>
<th>Si/Al$^a$</th>
<th>Acid site density /μmol g$^{-1}$</th>
<th>Particle size$^c$</th>
<th>Crystallite size$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>from ICP-OES$^b$</td>
<td>from NH₃-TPD</td>
<td></td>
</tr>
<tr>
<td>HZSM-5-55</td>
<td>55</td>
<td>298</td>
<td>308</td>
<td>179</td>
</tr>
<tr>
<td>HZSM-5-115</td>
<td>115</td>
<td>144</td>
<td>148</td>
<td>228</td>
</tr>
<tr>
<td>HZSM-5-651</td>
<td>651</td>
<td>25.6</td>
<td>27.3</td>
<td>218</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>HZSM-5-1119</td>
<td>1119</td>
<td>14.9</td>
<td>-</td>
<td>203</td>
</tr>
<tr>
<td>HZSM-5-1580</td>
<td>1580</td>
<td>10.5</td>
<td>-</td>
<td>213</td>
</tr>
</tbody>
</table>

\[ a \] Estimated from ICP-OES elemental analysis.

\[ b \] Assuming one Brønsted acid site per aluminum atom in the framework.

\[ c \] Estimated from TEM imaging.

\[ d \] Estimated from 2,2-dimethylbutane adsorption uptake measurements

**Figure 3.1.** NH₃ temperature programmed desorption measurements (NH₃-TPD) for HZSM-5-55, HZSM-5-115, and HZSM-5-651.
Figure 3.2. X-ray diffraction patterns of as-synthesized zeolite samples. And a simulated XRD pattern of ZSM-5-type zeolite framework is also shown for comparison.

Figure 3.3. TEM images and the particle-size distribution of (a) HZSM-5-55, (b) HZSM-5-115, (c) HZSM-5-257, (d) HZSM-5-1119, and (e) ZSM-5-1580.
The textural properties of the as-gained HZSM-5 samples were then estimated by Ar adsorption-desorption measurements. The Ar adsorption-desorption isotherms of the as-synthesized HZSM-5 samples collected at 87 K are presented and the evaluated textural characteristics are summarized in the Figure 3.4 and Table 3.2. The calculated results show that the as-synthesized HZSM-5 samples all have similar total surface area ($S_{BET}$) (412 – 443 m$^2$ g$^{-1}$), micropore surface area ($S_{Micpore}$) (379 – 415 m$^2$ g$^{-1}$), total pore volume (TPV) (0.172 – 0.199 cm$^3$ g$^{-1}$), and micropore volume ($V_{Micpore}$) (0.125 – 0.140 cm$^3$ g$^{-1}$).

![Figure 3.4. Ar adsorption (filled symbols)-desorption (open symbols) isotherms of HZSM-5-55, HZSM-5-115, HZSM-5-651, HZSM-5-1119, and HZSM-5-1580 at 87 K.](image)
**Table 3.2.** Summary of the textural characteristics of HZSM-5 samples.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>TPV (cm$^3$/g)</th>
<th>$V_{\text{micpore}}$ (cm$^3$/g)</th>
<th>$S_{\text{Micpore}}$ (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5-55</td>
<td>412</td>
<td>0.199</td>
<td>0.132</td>
<td>379</td>
</tr>
<tr>
<td>HZSM-5-115</td>
<td>439</td>
<td>0.188</td>
<td>0.136</td>
<td>408</td>
</tr>
<tr>
<td>HZSM-5-651</td>
<td>443</td>
<td>0.196</td>
<td>0.140</td>
<td>415</td>
</tr>
<tr>
<td>HZSM-5-1119</td>
<td>427</td>
<td>0.172</td>
<td>0.126</td>
<td>401</td>
</tr>
<tr>
<td>HZSM-5-1580</td>
<td>419</td>
<td>0.173</td>
<td>0.129</td>
<td>395</td>
</tr>
</tbody>
</table>

BET surface area was calculated by BET method under the absorption pressure $p/p_0 < 0.05$.

Total pore volume (TPV) was measured at the absorption pressure $p/p_0 = 0.95$.

The volume and surface area of micropores (< 1.5 nm) were calculated by DFT method.

### 3.3.2. Adsorption uptake measurements of 2,2-dimethylbutane

The average crystallite sizes for all of the as-synthesized HZSM-5 samples were then estimated by the adsorption uptake of 2,2-dimethylbutane (2,2-dmb) at 25 °C and 13 – 15 kPa 2,2-dmb partial pressure. The MFI-type zeolite topology consists of sinusoidal-channels (0.54 nm × 0.56 nm) and intersecting straight-channels (0.51 nm × 0.55 nm). The kinetic diameter of the probe molecule 2,2-dmb is 0.63 nm, which is very close to the size of the pore-openings of MFI. The uptake rate of 2,2-dmb could thus be applied
to estimate the crystallite size of the zeolites with MFI-type topology.\textsuperscript{60} The theoretical adsorption capacity of ZSM-5 on 2,2-dmb, which adsorbs preferentially in the channel intersections of MFI zeolite, is 4 2,2-dmb molecules per MFI unit cell or ~60 mg g\(^{-1}\).\textsuperscript{148}

In Figure 3.5 the adsorption uptakes of 2,2-dmb on ZSM-5 samples at 20 °C and 13 – 15 kPa 2,2-dmb pressure were then shown. The amount of 2,2-dmb adsorbed on samples was first normalized to the theoretical adsorption capacity of 2,2-dmb in ZSM-5 zeolite. Assuming a spherical crystallite (with a diameter equal to the crystallite size of the zeolite), a simple Fickian diffusion model can then be applied to describe the uptake behavior of 2,2-dmb in ZSM-5. As the isothermal conditions and in the absence of any other transport restriction, the concentration profile of a probe molecule inside the zeolite crystallite can be given by Equation 1,\textsuperscript{149-150}

\[
\frac{C(r,t)}{C_{\infty}} = 1 + \frac{2R}{\pi r} \sum_{n=1}^{n=\infty} \left[ \frac{(-1)^{n}}{n} \sin \left( \frac{n\pi r}{R} \right) \exp \left( -\frac{D_{\text{eff}} n^2 \pi^2 t}{R^2} \right) \right] 
\] (Eq. 1),

where \(C(r,t)\) is the concentration of probe 2,2-dmb inside of the spherical zeolite particle, \(r\) is the radial co-ordinate, \(t\) is the temporal coordinate, \(D_{\text{eff}}\) is the effective diffusivity of probe 2,2-dmb in MFI framework at 25 °C, and \(C_{\infty}\) is the saturation capacity of 2,2-dmb in ZSM-5 samples.
Figure 3.5. Adsorption uptake of 2,2-dimethylbutane (2,2-dmb) on HZSM-5-55 (□), HZSM-5-115 (△), HZSM-5-651 (◆), HZSM-5-1119 (○), and HZSM-5-1580 (►), at 298 K and 13 – 15 kPa 2,2-dmb pressure. The adsorbed amount was normalized to the theoretical adsorption capacity of 2,2-dmb in ZSM-5. The solid lines represent the fits for the experimental data using Eq. 2.

The adsorbed amount of 2,2-dmb inside of the zeolite can thus be obtained from Eq. 1 by integrating C(r,t) between r = 0 and r = R,\(^{149-150}\)

\[
\frac{M_t}{M_{\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left[ \frac{1}{n^2} \exp\left( - \frac{D_{\text{eff}} n^2 \pi^2 t}{R^2} \right) \right] \tag{Eq. 2}
\]

where \(M_t\) and \(M_{\infty}\) are the adsorbed amount at time \(t\) and at saturation state, respectively. Eq. 2 (from \(n = 1\) to \(n = 100\)) was fitted to the experimental data and six
parameters – the crystallite size of each ZSM-5 sample as well as the diffusivity of 2,2-dmb in ZSM-5 zeolite at 25 °C – were then estimated. The calculated crystallite sizes of all the ZSM-5 zeolite samples are reported in Table 3.1 (as shown in the above discussion part of this chapter). The effective diffusivity $D_{\text{eff}}$ of 2,2-dmb was calculated to be $3 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$ on ZSM-5 at 25 °C. We have to mention that this value is similar to the values which are reported previously by Khare et al. $^\text{60} \sim 9 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$, Cavalcante and Ruthven et al. $^\text{151} \sim 1 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$, and Xiao et al. $^\text{152} \sim 4 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$.

### 3.3.3. Effects of aluminum content on ethylene selectivity in MTH conversion

DME (dehydrated form of methanol) (at 49 – 57 kPa pressure) was reacted on HZSM-5 catalysts at 350 °C and 103 – 106 kPa total feeding pressure. The DME weight hourly space velocity (WHPV) was varied between 0.3 – 2.5 mol C (mol Al-s)$^{-1}$ to achieve an isoconversion (46 – 52% net DME conversion). Figure 3.6 shows the ethylene selectivity, propylene selectivity, and the ratio of ethylene/2MBu, as a function of the silicon-to-aluminum ratios. And a detailed product distribution is also shown in the Table 3.3. We found that the ethylene selectivity was decreased monotonically from 16% to 5.7%, and the total light olefins selectivity was decreased from 38% to 23% as the Si/Al ratios increased from 55 to 1580. The ratio of Ethylene/2MBu was also decreased monotonically from 2.4 to 0.80 with increasing the Si/Al ratios, indicating that a preferential propagation of aromatics-based catalytic cycle was occurred in HZSM-5 sample with a lower Si/Al ratio (or higher aluminum content). These results then support our postulate before that a decrease in Si/Al ratio or an increase in Al content
could enhance the propagation of the aromatics-based catalytic cycle and consequently results in higher ethylene selectivity. It must be noted that a higher concentration of acid site in the zeolite may first increase the concentration of aromatics formed inside of the zeolite which was mediated by a higher probability of sequential chain growth, ring closure, and hydride transfer reactions as required to produce aromatics, and/or secondly increase the probability that an aromatics will interact with the acid sites before it diffuses out from the zeolite crystallite. Both of these two effects will result in a higher propagation of the aromatics-based cycle and thus an increased selectivity to ethylene during the reaction.
Figure 3.6. Ethylene selectivity (■), propylene selectivity (□), and ethylene/2MBu (◇), for DME conversion on HZSM-5 samples with similar crystallite size (150 – 240 nm) and Si/Al varying between 55 and 1580 at 350 °C, 49 – 57 kPa DME pressure, and 46 – 52% iso-conversion.

Table 3.3. Reaction conditions and selectivity, on a carbon basis, towards C₂, C₃, C₄–C₇ hydrocarbons, methylbenzenes, and Others fraction for the reaction of DME on HZSM-5 samples with similar crystallite size (150 – 240 nm) and Si/Al varying between 55 and 1580 at 350 °C, 49 – 57 kPa DME pressure, and 46 – 52% iso-conversion conditions.

<table>
<thead>
<tr>
<th>Si/Al in the HZSM-5 samples</th>
<th>55</th>
<th>115</th>
<th>651</th>
<th>1119</th>
<th>1580</th>
</tr>
</thead>
<tbody>
<tr>
<td>DME pressure /kPa</td>
<td>55</td>
<td>57</td>
<td>54</td>
<td>51</td>
<td>49</td>
</tr>
<tr>
<td>Total feed pressure /kPa</td>
<td>104</td>
<td>105</td>
<td>106</td>
<td>103</td>
<td>104</td>
</tr>
</tbody>
</table>
Space-velocity /mol C (mol Al-s)$^{-1}$ | 0.36 | 2.40 | 3.98 | 3.23 | 2.80
Net carbon converted /% | 47 | 48 | 48 | 46 | 52

**Product selectivity (on a carbon basis), %**

<table>
<thead>
<tr>
<th></th>
<th>C$_2$</th>
<th></th>
<th>C$_3$</th>
<th></th>
<th>C$_4$–C$_7$</th>
<th></th>
<th>MBs</th>
<th></th>
<th>Others$^a$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15.9</td>
<td>11.6</td>
<td>7.8</td>
<td>5.8</td>
<td>41.7</td>
<td>43.7</td>
<td>46.7</td>
<td>49.5</td>
<td>49.2</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>24.5</td>
<td>21.6</td>
<td>20.7</td>
<td>18.4</td>
<td>6.6</td>
<td>6.3</td>
<td>6.3</td>
<td>6.4</td>
<td>7.3</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
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<td></td>
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<td></td>
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</tr>
</tbody>
</table>

$^a$ Others fraction includes C$_8^+$ hydrocarbons except polymethylbenzenes.

### 3.3.4. A single-value descriptor of ethylene selectivity in MTH conversion

Previously, it has been documented that the ethylene selectivity during MTH conversion monotonically increases with increasing the crystallite size of ZSM-5-type zeolites. The results showed in section 3.3.3 show that ethylene selectivity also monotonically increased with increasing the Al content or decreasing the Si/Al ratio in ZSM-5 catalysts. The underlying mechanistic reason for these two effects is the enhancement of the propagation of the aromatics-based catalytic cycle owing to an increase of the number of interactions between the MBs and Brønsted acid sites before these large MB
molecules diffuse out from the zeolite crystallites. Decreasing Si/Al ratio (or increasing Al content) could enhance the number of interactions by the increase of the concentration of active acid sites. Increasing the crystallite size of catalyst, from the other side, increases the number of interactions by elongating the intra-crystalline residence time of intermediates MBs. These two effects can thus be combined together into a single-value descriptor (here referred to as \( N_{H^+} \)) of ethylene selectivity, which represents the average number of interactions between a MB molecule and a Brønsted acid site before the MB molecule diffuses out from the zeolite crystallite.

The average number of interactions between a MB molecule and an active site before it exits the zeolite crystallite will decrease with decreasing crystallite size and increase with decreasing Si/Al ratio in zeolite. \( N_{H^+} \) therefore must be proportional to the crystallite size (in nm) of zeolite and the Si/Al ratio of the material;

\[
N_{H^+} = \frac{\text{Crystallite size (in nm)}}{\text{Si/Al}}
\]  
(Eq. 3)

These assumptions involved in the formulation of \( N_{H^+} \) parameter are presented in greater detail in the supplementary Information section in our published work, and no more details are illustrated here.\(^{353}\) Based on this parameter, \textbf{Figure 3.7} shows the ethylene selectivity and 2MBu selectivity as a function of \( N_{H^+} \) for the conversion of DME on ZSM-5 samples at 350 °C, 49 – 66 kPa DME pressure, and 46 – 59% net DME conversion. The ethylene selectivity systematically increases with an increase in the value of \( N_{H^+} \) which supports our postulate before that the effects of aluminum content
and crystallite size on ethylene selectivity can be described by a construct that posits that the aromatics-based catalytic cycle propagates to a greater extent due to an increase in the interactions between MBs and acid sites. The results shown in Figure 3.7 are based on crystallite sizes derived from 2,2-dme adsorption uptake measurements for the calculation of $N_{H^+}$, however, the same trends are observed when crystallite sizes based on TEM data are used because that the close identical crystallite sizes (150 – 240 nm) of ZSM-5 samples are used in this investigation.

The extent of the propagation of the olefins-based catalytic cycle – represented by 2MBu selectivity – does not increase with increasing the $N_{H^+}$ parameter. Generally, the olefins have smaller kinetic diameters compared to the MBs molecules. For example, the kinetic diameter of isobutene is around $\sim 5.0 \text{ Å}^{154}$ while the kinetic diameter of 1,2,4-triMB is about $\sim 7.6 \text{ Å}^{155}$. The average intra-crystalline residence time of active MBs is thus longer than that of the olefins, which implies that an increase in the crystallite size affects the intra-crystalline residence time of MBs to a greater extent than that of olefins. Correspondingly, the enhancement of the propagation of the aromatics-based catalytic cycle is larger compared to the propagation of olefins-based catalytic cycle with the increase of $N_{H^+}$ parameter. In the olefins-based catalytic cycle, light olefins will methylate or oligomerize to form higher olefins which then undergo $\beta$-scission to form light olefins – these olefin-interconversion reactions render the selectivity of olefins largely invariant with the extent of the propagation of the olefins-based cycle.\textsuperscript{17, 72-74} In the aromatics-based catalytic cycle, however, MBs undergo methylation/dealkylation
reactions and produce ethylene (which is less reactive compared to the C$_3$+ olefins) without getting consumed themselves.$^{62-63, 81, 156}$ An increase of $N_{H+}$ enhances the propagation of both the catalytic cycles, but, the propagation of the aromatics-based catalytic cycle is enhanced to a larger extent relative to the propagation of the olefins-based catalytic cycle and therefore results in a higher selectivity to ethylene, as observed above experimentally.

$^{a}$ 2MBu = 2-methylbutane + 2-methyl-2-butene. A representative of the propagation of olefins-based catalytic cycle.

**Figure 3.7.** Ethene selectivity (filled symbols) and 2MBu$^{a}$ selectivity (open symbols) as a function of $N_{H+}$ – ratio of crystallite size (in nm) and Si/Al – for DME conversion on HZSM-5 samples investigated in this work (■, □) and zeolite samples investigated in reference$^{60}$ (◆, ◇) at 623 K, 49 – 66 kPa DME pressure, and 46 – 59% DME iso-conversion.
3.4. Conclusions

In this chapter, we prepared a series of ZSM-5 zeolites with different Si/Al ratios (ranging from 55 to 1580), but similar crystallite sizes (around 150 – 240 nm), in order to investigate the influence of Al content on the product distribution during the MTH reaction. Results for the ethylene selectivity, during MTH reaction at 350 ºC and 46 – 52% DME iso-conversion on five ZSM-5 samples decreased from 16% on ZSM-5 with high aluminum content (Si/Al = 55) to 5.7% on the that one with low aluminum content (Si/Al = 1580). The mechanistic reason for this decreasing trend on ethylene selectivity with decreasing aluminum content is a decrease in the number of interactions between the active sites and methylbenzenes before these methylbenzene molecules diffuse out from the zeolite crystallites. The parameter Ethylene/2MBu also monotonically decreased from 2.4 on ZSM-5 sample with high aluminum content (Si/Al = 55) to 0.8 on ZSM-5 sample with low aluminum content (Si/Al = 1580). A single-value descriptor representative of the average number of active sites that a methylbenzene molecule encounters before it exits the zeolite crystallite describes the combined effects of aluminum content and crystallite size on ethylene selectivity for MTH reaction on the MFI-type zeolites.
Chapter 4: Investigation into the role of olefins-based catalytic cycle for propylene formation during methanol-to-olefins conversion over DDR

4.1 Introduction

The conversion of methanol-to-hydrocarbons (MTH) has attracted considerable attention in the past few decades, because it was considered as a new way to produce fuels and chemicals independent of petroleum-based synthetic routes. According to the product distributions, the MTH reaction can be classified into the following categories, methanol-to-olefins (MTO)\textsuperscript{54, 157-159}, methanol-to-gasoline (MTG)\textsuperscript{15, 160}, methanol-to-propylene (MTP)\textsuperscript{22, 24, 161} and methanol-to-aromatics (MTA)\textsuperscript{25, 162-165}. The product distributions are generally determined by the reaction conditions and the structure of zeolites. In order to achieve the product distribution control, many efforts have been devoted to clearly and deeply understanding the mechanism of the MTH reaction. Extensive research has shown that the MTH reaction proceeds through an indirect “hydrocarbon pool” mechanism with two competitive catalytic cycles,\textsuperscript{17-18, 57, 65, 129, 156} in which the aromatics-based active intermediates and olefin-based hydrocarbon pool species repeatedly undergo methylation, dealkylation or β-scission reactions to produce the complex hydrocarbons. The complicated product distributions can be clearly summarized by the emergence of the dual catalytic cycle mechanism. For example, ZSM-22 has one-dimensional non-interacting 10-member-ring channels that are too small to form polymethylbenzenes intermediates, which suppresses the aromatics-
based cycle, and thus the olefin-based cycle is relatively promoted in the conversion process, resulting in high selectivity for branched C₅+-fraction alkenes.⁵⁸-⁵⁹ In ZSM-5 samples with different diffusion length, the ethylene and total olefin selectivity increase with the effective crystallite size, owing to the promoted propagation of the aromatics-based cycle as a result of prolonged intra-crystalline residual time of methylbenzenes.⁶⁰

And also, increasing the methanol partial pressure could favor the hydrogen transfer process, and thus enhance the aromatics-based cycle with a high selectivity toward ethylene.⁶¹

Zeolite topology with small-pore frameworks is highly selective to lower olefins (ethylene and propylene, as high-value petrochemical building blocks), because the large organic species formed in the catalytic process cannot exit from the small pore openings. Most of the recent researches on MTO conversion are focused on the commercial catalyst, small-pore SAPO-34 zeolite. And it was generally recognized that aromatics-based species are identified as the active intermediates for light olefins formation in MTO conversion over small pore zeolites, because the small windows can easily trap the large aromatic intermediates. By isotopic switching (¹²CH₃OH/¹³CH₃OH) experiments, Hereijgers and coworkers provided evidence that methylbenzenes are the active intermediates comprising the aromatics-based hydrocarbon pool, and predominantly contributed to the formation of ethylene, propylene and butene.¹²⁸

With the aid of GC-MS and ssNMR technologies, Li and coworkers directly observed the active hexamethylenecyclohexadiene (HMMC) species and heptamethylbenzenium
cation (heptaMB⁺) in SAPO-type DNL-6. By operando UV–vis spectroscopy, Weckhuysen’s group revealed that the major active hydrocarbon pool species during MTO reaction on CHA zeolites (i.e. SSZ-13 and SAPO-34) are methylated aromatic species. Via ¹H and ¹³C MAS NMR spectroscopy, Dai and coworkers found several species (like three-ring compounds, dienes, polymethylcyclopentenyl and polymethylcyclohexenyl cations) in SAPO-34 at the initial time of MTO reaction, and they proposed that these olefins-like species evolved to the aromatics-based intermediates at the steady-state of the reaction. However, they didn’t provide any evidence that these olefins species are the active intermediates for the production of light olefins. Very recently, by isotopic tracing experiments, Bhan’s group demonstrated the operation of the olefins-based cycle at early turnover numbers in MTO conversion with SAPO-34. But they also found that this olefins-based cycle would be impeded by the inevitable accumulation of aromatics that facilitates the propagation of the aromatics-based cycle with catalyst turnover.

Despite great progress has made on the mechanism of MTO conversion over small-pore zeolites, the role of olefins-based hydrocarbon pool is rarely studied and its influence on the product distribution remains unclear. As to our knowledge, only by extensive periodic density functional theory (DFT) calculations, Xie et al. suggested that olefins themselves could be the dominating hydrocarbon pool species contributing to the selectivity of ethylene and propylene in MTO conversion. In this study, we experimentally explored the role of olefins-based cycle in the MTO reaction with small-
pore DDR zeolite. We endeavor to solve the important question on the MTO reaction, how and by what the selectivity of ethylene and propene is controlled based on the dual cycle mechanism? DDR topology was identified as a promising 8-ring zeolite structure for the MTO process. Followed by the preparation of series different structured DDR zeolites (with different Si/Al ratios or diffusion lengths), we then evaluate the performances of the catalysts at sub-complete methanol conversion in which both the catalytic cycles are supposed to occur. We found that during the MTO process over DDR zeolite, the preferential propagation of the olefins- or aromatics-based cycles contributes to the selectivity of propylene or ethylene, respectively. The mechanistic reason for the role of olefins-based cycle on the formation of propylene is the confinement effect of the small pores on the higher olefins’ transportation.

4.2 Experimental

4.2.1 Synthesis of DDR (Sigma-1) with different Si/Al ratios

DDR (Sigma-1) zeolite catalysts were synthesized via hydrothermal synthesis according to a previously reported method with minor modifications. In a typical synthetic process of DDR with a Si/Al ratio of ~25, 1.8 g of SiO$_2$ in Ludox SM-30 was added to vial A and was diluted with 4.57 g of H$_2$O. After 5 min of stirring, 0.905 g of ADA in 4.85 g of H$_2$O was added and the obtained solution was further stirred for over 15 min until a homogenous solution was obtained. In vial B, firstly 0.05 g of NaAlO$_2$ was dissolved in 1.35 g of H$_2$O. After obtaining a clear solution, 0.048 g of NaOH in 1 g of H$_2$O was added.
After stirring vial B for 15 min, vial B is mixed over vial A and aging was continued for 30 min. The gained solution was transferred to Teflon containers and synthesis was carried out at 180 °C under autogenous pressure for 6.5 days under 20 rpm of rotational speed. The products were recovered by centrifugation, washed several times with deionized water, and dried in air. The obtained powder was treated in dry air at 550 °C for 16 h to remove the organic structure-directing agent. For the synthesis of DDR with different Si/Al ratios, the amount of NaAlO₂ in the synthetic precursor was adjusted accordingly with other conditions unchanged. These samples are here referred to as DDR_X, where X corresponds to a Si/Al ratio as determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). To convert zeolites to the H-form, the as-synthesized zeolite powder was overnight ion-exchanged with a 0.5 M NH₄NO₃ solution (20 mL per gram of zeolite) for three times, dried in air at 70 °C, and then calcined at 550 °C in air for 4 h. The obtained samples were then pressed into pellets, crushed, and sieved between 100- and 300-mesh sieves to obtain uniform particles with size between 50 and 150 µm.

DDR (Sigma-1) zeolite catalysts with hierarchical structures were synthesized with post-treatment method. The as-synthesized DDR samples (0.5 g) were treated with 10 mL 0.2 M NaOH at 75 °C for 1 h, followed by the treatment with 10 mL 0.1 M HCl at 70 °C for 1 h. The gained materials were named as DDR_X* (X corresponds to an original Si/Al ratio). To convert zeolites to the H-form, the as-synthesized zeolite powder was overnight ion-exchanged with a 0.5 M NH₄NO₃ solution (20 mL per gram of zeolite) for
three times, dried in air at 70 °C, and then calcined at 550 °C in air for 4 h. The obtained samples were then pressed into pellets, crushed, and sieved between 100- and 300-mesh sieves to obtain uniform particles with size between 50 and 150 µm.

**4.2.2 Characterizations of the catalysts**

The powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer using Cu Kα radiation. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was conducted on a Varian 720-ES spectrometer. Scanning Electron Microscopy (SEM) images were acquired on a Nova Nano 630 SEM operated at 3 Kv. Ar adsorption-desorption isotherms were measured on a Micromeritics 3 Flex Surface Characterization Analyzer at 87 K, with the sample degassed at 400 °C under high vacuum for 8 h. The total surface area was calculated by the Brunauer–Emmett–Teller (BET) method. Total pore volume was measured at the absorption pressure P/P₀ = 0.95, and the micropore volume (<1.5 nm) was estimated using the NLDFT method.

Adsorption uptake of propylene was measured at 50 °C to estimate the average crystallite size of the synthesized DDR samples. Adsorption of Propene was performed on a Micromeritics ASAP 2020 surface area and porosity analyzer. Prior to analysis, the catalyst sample (~20 mg) was outgassed at 400 °C for 8 h under high vacuum. The adsorption data were collected at 50 °C and 5 – 10 kPa propene pressure.

Temperature-programed desorption (TPD) measurements using NH₃ as the probe molecule were performed on a Micromeritics AutoChem II 2950 apparatus. Before
measurements, 0.10 g of the sample was pretreated in He gas (25 ml/min) for 2 h at 500 °C and then cooled to 100 °C. Next, the sample was exposed to a mixed gas (10 mol% NH₃ and 90 mol% He) flow of 20 mL/min for 0.5 h to ensure the sufficient adsorption of NH₃. Prior to desorption, the sample was flushed in He gas for 3 h. Subsequently, NH₃ desorption was performed in the range of 100 – 600 °C at a heating rate of 10 °C /min under a He flow of 20 mL/min.

4.2.3 Catalytic reactions

MTH conversion was performed in a quartz fixed-bed reactor (1/4 in OD; 0.5 mm in wall thickness) packed with certain amount of zeolite catalyst. The catalyst bed was activated in a pure air flow (20 mL/min) at 500 °C for 60 min prior to each run, after which the temperature was decreased to the reaction temperature (400 °C and 450 °C), and the air flow was switched to He (15 – 20 mL/min) gas flow mixed with a certain flow rate of methanol using a HPLC pump, and the pressure of MeOH is around 3.6 – 7.8 kPa. The desired methanol conversions were achieved by adjusting the weight hourly space velocity (WHSV) in the range of 1.6 to 11.5 gₘₑₒₙ g⁻¹ Cat⁻¹ h⁻¹. The reactions were all performed under atmospheric pressure, and the product was analyzed using online gas chromatography. Composition of the effluent was determined by gas chromatography (GC) with a flame ionization detector equipped with Agilent HP-PLOT/Q column (30 m*0.53 mm*40 μm); dimethyl ether was not considered as a product for the calculation.
4.2.4 $^{12}\text{C}/^{13}\text{C}$ methanol switch experiments

In the $^{12}\text{C}/^{13}\text{C}$ methanol switch experiments, the $^{12}\text{C}$ methanol was first fed for 10 min at 400 °C, and then the feeding line was switched to $^{13}\text{C}$ methanol (Sigma-Aldrich) and reacted further for a predetermined time. The time evolution of the $^{13}\text{C}$ content in the effluent was tested in GC-MS analyses performed 0.5, 1.0, 2.0, 3.0 and 4.0 min after the $^{12}\text{C}/^{13}\text{C}$ methanol switch. Corresponding $^{13}\text{C}$ content for the organic species retained in the zeolite pores during reaction were obtained from the parallel experiments by thermally quenching the reaction after 1.0, 2.0, 3.0 and 4.0 min of $^{13}\text{C}$ methanol reaction.

4.2.5 Analysis of the residual organic species in used catalysts

Residual soluble organic species from catalysts were extracted following a commonly used procedure.\textsuperscript{101-102, 133} Specifically, the catalyst was taken out of the reactor after the desired reaction time, and this used catalyst was transferred to a capped Teflon vial and dissolved in 6 mL of 24 % HF for 3 h. Then, 6.0 mL of CH\textsubscript{2}Cl\textsubscript{2} was added to the solution to extract the liberated organic species from the water phase. After 3 h, the organic phase was separated from the mixture, and analyzed using GC–MS equipped with Agilent PONA column (50 m*0.2 mm*0.5 μm).
4.3 Results and discussion

4.3.1 Structural and chemical characterization

According to the literature, three zeolites belong to the DDR family, DD3R (pure silica version) and two Al-containing variants, Sigma-1 and ZSM-58. Both DD3R and Sigma-1 are synthesized using adamantylamine (ADA) as the structure directing agent (SDA), while methyltropinium iodide is employed for ZSM-58 synthesis. In our work, the DDR zeolites with Sigma-1 type structure were synthesized according to a previously reported method with slight modification.\(^{168}\) The X-ray diffraction patterns of the synthesized DDR (Sigma-1) samples together with reference peaks for DDR topology are presented in Figure 4.1 and demonstrate that the synthesized samples are crystalline with a pure DDR-type framework. Ar adsorption-desorption isotherms of the synthesized DDR samples are collected at 87 K (As shown in Figure 4.2) and the evaluated textural properties are summarized in Table 4.1. The results show that the synthesized materials have similar total surface area (248 – 296 m\(^2\)/g), micropore surface area (189 – 234 m\(^2\)/g), total pore volume (0.140 – 0.173 cm\(^3\)/g), and micropore volume (0.078 – 0.097 cm\(^3\)/g). The Si/Al ratios of the synthesized DDR samples were determined from the ICP-OES elemental analysis and their acid densities were determined from NH\(_3\)-TPD measurements. NH\(_3\)-TPD results (in Figure 4.3) show that the acid density and the acid strength are both decreased with the increase of the Si/Al ratios in DDR samples. This result is consistent with their Si/Al ratios tested by ICP-OES.
method (in table 4.2), suggesting nearly complete incorporation of Al in the zeolite framework in these samples.

**Figure 4.1.** XRD patterns of as-synthesized DDR zeolites with different Si/Al ratios.

**Figure 4.2.** Ar adsorption isotherms of nano-sized DDR zeolites with different Si/Al ratios.
### Table 4.1. Textural properties of DDR zeolites with different Si/Al ratios and diffusion length.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al Ratio</th>
<th>( S_{\text{BET}} )(^{b})</th>
<th>Total Volume(^{c})</th>
<th>( V_{\text{Micpore}} )(^{d})</th>
<th>( V_{\text{Ext}} )(^{e})</th>
<th>( S_{\text{Micpore}} )(^{f})</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDR_22</td>
<td>22:1</td>
<td>276</td>
<td>0.147</td>
<td>0.088</td>
<td>0.059</td>
<td>230</td>
</tr>
<tr>
<td>DDR_43</td>
<td>43:1</td>
<td>296</td>
<td>0.173</td>
<td>0.097</td>
<td>0.076</td>
<td>234</td>
</tr>
<tr>
<td>DDR_87</td>
<td>87:1</td>
<td>263</td>
<td>0.140</td>
<td>0.085</td>
<td>0.055</td>
<td>228</td>
</tr>
<tr>
<td>DDR_172</td>
<td>172:1</td>
<td>248</td>
<td>0.148</td>
<td>0.078</td>
<td>0.070</td>
<td>189</td>
</tr>
<tr>
<td>DDR_172*</td>
<td>168:1</td>
<td>213</td>
<td>0.138</td>
<td>0.053</td>
<td>0.085</td>
<td>143</td>
</tr>
</tbody>
</table>

\(^{a}\) Si/Al ratio was tested by ICP-OES.

\(^{b}\) BET surface area was calculated by BET method under the absorption pressure \( p/p_0 < 0.05 \).

\(^{c}\) Total pore volume was measured at the absorption pressure \( p/p_0 = 0.95 \).

\(^{d}\) The volume of micropores (< 1.5 nm) was calculated by DFT method.

\(^{e}\) The external pore volume was calculated by the total volume substrates the volume of micropores.

\(^{f}\) Surface area of micropores was calculated by DFT method.

\(^{g}\) Surface area of external pores was calculated by the BET surface area substrates the micropore’s surface area.
4.3.2 Adsorption uptake measurements of propylene

An effective crystallite size for each of the synthesized DDR samples was estimated from the adsorption uptake of propylene at 50 °C. The pore size of DDR-type zeolite framework is 3.6 × 4.4 Å, and propylene is usually used as adsorbate to test the diffusion property. Figure 4.4 shows the adsorption uptake of propylene on DDR samples at 50 °C. Assuming spherical crystallites (with diameter, 2R, equal to the crystallite size of the zeolite), a simplified equation (1) from Fick’s second law can be used to estimate the crystallite size of DDR zeolites by the uptake rate of propylene,

\[
\frac{M_t}{M_\infty} = \frac{6}{\sqrt{\pi}} \sqrt[3]{\frac{D_{\text{eff}} t}{R^2}}
\]

where \(M_t\) and \(M_\infty\) are the adsorbed amount at time t and at saturation respectively, and \(D_{\text{eff}}\) is the effective diffusivity of propylene in DDR framework at 50 °C. The effective
diffusivity ($D_{\text{eff}}$) $5 \times 10^{-12}$ cm$^2$s$^{-1}$ on DDR at 50 °C from previous report was used here and the estimated parameters reported in Table 4.2 confirm that the crystallite sizes of the investigated DDR samples are similar (534 – 634 nm). SEM images of the as-synthesized DDR samples (Figure 4.5) also confirm that the synthesized samples have nearly identical particle sizes despite the variable Al contents. The diffusion length has been proved as an important effect on the mechanism of MTH reaction. In this study, we also synthesized a hierarchically structured DDR zeolite (DDR_172*), which was post-treated from DDR_172 sample, and it shows a shorter diffusion length than its mother sample tested by the adsorption uptake measurements (Figure 4.6).

**Table 4.2**, Si/Al ratios and crystallite sizes of DDR samples investigated in this work.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al ratio $^a$</th>
<th>Acid site density $^b$ (mmol g$^{-1}$)</th>
<th>Diffusion parameter $^c$, $D_{\text{eff}}/R^2$ (s$^{-1}$)</th>
<th>$R^d$ (nm)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDR_22</td>
<td>22 : 1</td>
<td>0.644</td>
<td>0.0050</td>
<td>317</td>
<td>634</td>
</tr>
<tr>
<td>DDR_43</td>
<td>43 : 1</td>
<td>0.352</td>
<td>0.0025</td>
<td>445</td>
<td>890</td>
</tr>
<tr>
<td>DDR_87</td>
<td>87 : 1</td>
<td>0.194</td>
<td>0.0070</td>
<td>267</td>
<td>534</td>
</tr>
<tr>
<td>DDR_172</td>
<td>172 : 1</td>
<td>0.075</td>
<td>0.0068</td>
<td>271</td>
<td>542</td>
</tr>
<tr>
<td>DDR_172*</td>
<td>168 : 1</td>
<td>0.082</td>
<td>0.0353</td>
<td>119</td>
<td>238</td>
</tr>
</tbody>
</table>
a Si/Al ratio was tested by ICP-OES. b Estimated from NH$_3$-TPD analysis. c Estimated from propylene adsorption uptake measurements. d Calculated R values of DDR samples from propylene adsorption uptake measurements, D$_{eff}$ = $5 \times 10^{-12}$ cm$^2$ s$^{-1}$ (at 50 °C) was used from reference$^{169}$.

**Figure 4.4.** Adsorption uptake of propylene on DDR samples at 50 °C. The adsorbed amount of propylene normalized to saturated adsorption capacity versus the time on stream (a), and the square root of short time on stream (b).
Figure 4.5. SEM images of as-synthesized DDR zeolites with different Si/Al ratios (a, DDR_22 with Si/Al = 22; b, DDR_43 with Si/Al = 43; c, DDR_87 with Si/Al = 87; and d, DDR_172 with Si/Al = 172), the scale bar is 10 µm in all images.
Figure 4.6. (a) SEM image of DDR_172* (Synthesized from DDR_172 by desilication and dealumination). (b) Adsorption uptake of propylene on DDR samples at 50 °C. The adsorbed amount of propylene normalized to saturated adsorption capacity versus the square root of short time on stream. (c) XRD pattern of DDR_172*. (d) Ar adsorption isotherms of DDR_172*.

4.3.3 Effects of aluminum content on product distribution in MTO conversion

Besides SAPO-34, other small-pore zeolites (like SSZ-13, DDR, LEV et al.) have also been identified as interesting candidates in MTO conversion. The as-synthesized DDR samples
for MTO conversion was performed here in a quartz fixed-bed reactor at 400 °C and 450 °C, with the pressure of MeOH around 3.6 – 7.8 kPa. The weight hourly space velocity (WHSV) was varied in the range of 1.6 to 11.5 g\textsubscript{MeOH} g\textsubscript{Cat}^{-1} h^{-1}, to achieve a net MeOH iso-conversion of 45 – 55%.

Trends in steady-state selectivity during MTO reaction on DDR zeolites help to reflect the trends in the relative propagation of the aromatics versus olefins-based catalytic cycle. Figure 4.7 shows the product distribution as a function of DDR samples with different Si/Al ratios at 400 °C and 450 °C. It is obviously to see that ethylene selectivity decreased monotonically from 36.6 % to 27.8 % at 400 °C and from 46.2 % to 37.9 % at 450 °C as Si/Al increased from 22 to 172. It was well demonstrated that the formation of ethylene is prevalingly from aromatics-based dealkylation events and negligibly from olefins-based β-scission at sub-complete methanol conversion. Kinetic studies also revealed that ethylene is relatively inert towards methylation compared to propylene, and thus ethylene was considered as the indicator of aromatics-based catalytic cycle in MTH. The trend of ethylene selectivity indicates that preferential propagation of the aromatics-based catalytic cycle occurred in DDR samples with higher aluminum content. This phenomenon is analogous to our recent report on ZSM-5 zeolite. Cooperated with Bhan’s group, we recently demonstrated that an increase in Al content (or decrease in Si/Al ratio) increases the propagation of the aromatics-based catalytic cycle in ZSM-5 zeolite and consequentially results in higher ethylene selectivity similarly. We contributed to the reasons as that high acid density increases the concentration of
aromatics within the zeolite, and also increases the probability that methylbenzenes interact with the acid sites before they exit the zeolite crystallite.\(^{153}\) However, in this investigated zeolite here, large-sized methylbenzenes can’t exit from the small-pore openings in DDR topology, so the only reason could be that a higher Al content facilities the formation of aromatics and increases the concentration of methylbenzenes inside of DDR zeolite. Paraffins are usually termed as hydrogen transfer index (HTI), because they are prevalently accompanied with the formation of aromatics, which is a stoichiometric requirement for hydrogen-redistribution pathways during zeolite-catalyzed hydrocarbons conversion.\(^{77-79}\) As shown in Figure 4.7 and Table 4.3, an observed increase in the selectivity toward C\(_1\) – C\(_4\) paraffins with increasing Al content in DDR samples suggests that a higher Al content facilities the formation of aromatics at both investigated reaction temperatures.

However, in sharp contrast to the selectivity of ethylene, the selectivity toward propylene increased monotonically from 38.1 % to 48.3 % at 400 °C and from 36.4 % to 41.1 % at 450 °C with the increase of Si/Al from 22 to 172. And in DDR sample with shorter diffusion length (in DDR_172\(^*\)), in which the acid site density was further diluted, the selectivity toward propylene was further increased to 50.6 % at 400 °C and 43.6 % at 450 °C, with a further decrease of ethylene selectivity to 26.4 % at 400 °C and 35.4 % at 450 °C (as shown in Figure 4.7 and Table 4.3). The trend in the propylene selectivity on DDR zeolites with the change of Si/Al ratios is obviously distinct from that in ZSM-5 zeolites in our previous report.\(^{153}\) In that report, we claimed the trends on the selectivity
of light olefins (ethylene and propylene) are resulted from the propagation of aromatics-based catalytic cycle.\textsuperscript{153} And previously, it was also claimed that all olefins are formed from the same aromatics-based intermediates in MTO conversion over SAPO-34.\textsuperscript{128} However, this statement seems cannot explain our new findings here. The trend on propylene selectivity, which is in the opposite way to ethylene, confirms that the propylene is mainly formed from the other competitive route, i.e. olefins-based catalytic cycle, and Hwang et al. also demonstrated the possible existence of this catalytic cycle at early catalyst turnovers during MTO conversion over SAPO-34.\textsuperscript{166}

![Figure 4.7. Product distribution as a function of DDR samples with different Si/Al ratios (DDR_172* is post-treated from DDR_172 sample). Reaction conditions: at 400 °C (a) and 450 °C (b), 3.6 – 7.8 kPa MeOH partial pressure, 45 – 55% net MeOH conversion, and 10-min time on stream.](image)
Table 4.3. Product distribution over DDR samples at 400 °C and 450 °C, 3.6 – 7.8 kPa MeOH partial pressure, 45 – 55% net MeOH conversion, and 10-min time on stream.

<table>
<thead>
<tr>
<th>DDR samples</th>
<th>Ethylene</th>
<th>Propylene</th>
<th>E + P</th>
<th>C_{1-4} Paraffins</th>
<th>P/E</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>400 °C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DDR_22</td>
<td>36.6</td>
<td>38.1</td>
<td>74.7</td>
<td>14.0</td>
<td>1.0</td>
</tr>
<tr>
<td>DDR_43</td>
<td>30.9</td>
<td>44.2</td>
<td>75.1</td>
<td>11.5</td>
<td>1.4</td>
</tr>
<tr>
<td>DDR_87</td>
<td>31.3</td>
<td>46.7</td>
<td>78.0</td>
<td>8.3</td>
<td>1.5</td>
</tr>
<tr>
<td>DDR_172</td>
<td>27.8</td>
<td>48.3</td>
<td>76.1</td>
<td>8.1</td>
<td>1.7</td>
</tr>
<tr>
<td>DDR_172*</td>
<td>26.4</td>
<td>50.6</td>
<td>77.0</td>
<td>6.2</td>
<td>1.9</td>
</tr>
<tr>
<td><strong>450 °C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DDR_22</td>
<td>46.2</td>
<td>36.4</td>
<td>82.6</td>
<td>8.1</td>
<td>0.8</td>
</tr>
<tr>
<td>DDR_43</td>
<td>40.3</td>
<td>36.5</td>
<td>76.8</td>
<td>8.3</td>
<td>0.9</td>
</tr>
<tr>
<td>DDR_87</td>
<td>41.1</td>
<td>36.8</td>
<td>77.9</td>
<td>7.0</td>
<td>0.9</td>
</tr>
<tr>
<td>DDR_172</td>
<td>37.9</td>
<td>41.1</td>
<td>79.0</td>
<td>5.7</td>
<td>1.1</td>
</tr>
<tr>
<td>DDR_172*</td>
<td>35.4</td>
<td>43.6</td>
<td>79.0</td>
<td>5.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>

4.3.4 $^{12}$C/$^{13}$C methanol switch experiments

In order to reveal the reason for the different product distributions, different DDR samples were then subjected to $^{12}$C/$^{13}$C methanol switch experiments at 400 °C. $^{12}$C methanol was fed for 10 min before switching to $^{13}$C methanol and reacted further for a
predetermined time. The time evolution of the $^{13}$C content in the effluent was determined from GC-MS analyses performed 0.5, 1.0, 2.0, 3.0 and 4.0 min after the $^{12}$C/$^{13}$C methanol switch (as shown in Figure 4.8). In these experiments, we focused on the $^{13}$C content in the products of ethylene and trans-2-butene, because ethylene is the terminal product from aromatics-based catalytic cycle, and trans-2-butene is main product in the effluent as the indicator of olefin-based catalytic cycle. The $^{13}$C content in the products could help to reflect the competition between these two catalytic cycles. The differences on the product selectivity can thus be mechanistically rationalized as a consequence of the relative extents of the propagation of olefins- and aromatics-based catalytic cycles.

![Figure 4.8](image_url)

**Figure 4.8.** Time evolution of $^{13}$C content in the effluent (ethylene and trans-2-butene) after $^{12}$C/$^{13}$C-methanol feed switch over different DDR zeolites at 400 °C.

As shown by the data in DDR_22 and DDR_172, it is obvious that the aromatics-based catalytic cycle is much faster than the olefin-based catalytic cycle. It was demonstrated previously that aromatics-based species are the main active intermediates in MTO
conversion over small-pore zeolites.\textsuperscript{128} And it is even documented that methylbenzenes with different number of methyl groups favor different products.\textsuperscript{170} In this work, corresponding isotopic data for the methylbenzenes retained in DDR zeolite pores were also obtained from the parallel experiments (as shown in Figure 4.9), showing the activity of the similar methylbenzenes (Penta- and Hexa-MBs) in the aromatics-based catalytic cycle. However, from this experiment, we revealed the role of olefin-based catalytic cycle in the MTO reaction over the small-pore DDR zeolite. The gap between the \textsuperscript{13}C content in these two products is remarkably lower in DDR_172 sample than that in DDR_22 sample. If we consider this gap value as how faster the aromatics-based catalytic cycle than the olefin-based catalytic cycle in MTO reaction, we can get the conclusion that DDR zeolite with high Si/Al ratio (or low Al content) favors the olefin-based catalytic cycle in MTO conversion. This conclusion is consistent with our report on ZSM-5 series samples and other reports as well. And furthermore, when comparing the results between DDR_172 and DDR_172* samples, in DDR_172* catalyst with a shorter diffusion length, olefin-based catalytic cycle is more favored than that in DDR_172 catalyst. Combining the propylene selectivity talked above, we can confirm that with the enhancement of the olefin-based catalytic cycle, the selectivity toward propylene is promoted in small-pore DDR zeolite during the MTO conversion. Usually, the C\textsubscript{4} - C\textsubscript{7} aliphatics are considered as the indicators of the olefins-based catalytic cycle, which will be promoted with the propagation of this catalytic cycle. However, owing to the confinement effect from the small pores, large olefins are easily restricted in the cage of DDR zeolites, and then they continue to follow the \(\beta\)-scission process to produce light
olefins, mainly for propylene. During MTH reactions, olefin cracking as an effective route to produce light olefins has already been proposed by Dessau and LaPierre,\textsuperscript{72-73} and it was thought as an important route to increase the production of propylene in Lurgi’s methanol-to-propene (MTP) process over ZSM-5 zeolite.\textsuperscript{17} Most recently, it was also demonstrated that in the high-Si large pore Beta zeolite, the olefins-based catalytic cycle contributes to the high propylene selectivity during the conversion of methanol.\textsuperscript{94, 171}

![Figure 4.9](image)

**Figure 4.9.** Time evolution of $^{13}$C content in the remained species after $^{12}$C/$^{13}$C-methanol feed switch over different DDR zeolites at 400 $^\circ$C.

### 4.3.5 Analysis of the residual organic species in used catalysts

To gain more information on what kinds of active intermediates remained inside of DDR catalysts, we extracted these organic species by the standard method: dissolution of the zeolite aluminosilicate framework with HF solution followed by extraction of the organic species with $\text{CH}_2\text{Cl}_2$ from the water phase. The soluble species, which are essentially the H-rich compounds residing in the zeolitic cages were analyzed with GC-MS. As shown in **Figure 4.10**, the relative proportions of methylbenzenes (MBs) and long-chain aliphatics
differ greatly among these samples. The content of MBs remained in DDR samples decreases in this order: DDR_22 > DDR_172 > DDR_172*; this trend is the same to the decrease of ethylene selectivity, which reflects that the aromatics-based dealkylation of methylbenzenes contributes to the formation of ethylene. However, in sharp contrast, the decreasing of long-chain aliphatics content follows an opposite order: DDR_172* > DDR_172 > DDR_22. This trend is the same to the decrease of propylene selectivity, providing additional evidence that the olefin-based β-scission reactions mainly produce propylene in the MTO reaction on our studied DDR samples.

Figure 4.10. Residual hydrocarbon species extracted from the different used catalysts after the reaction. Reaction conditions: at 400 °C, 3.6 – 7.8 kPa MeOH partial pressure, 45 – 55% net MeOH conversion, and 10-min time on stream.
4.3.6 DFT calculation on the kinetic diameters of potential olefin products.

The confinement effect of the small openings in DDR topology was further investigated. Density Functional Theory (DFT) based calculations were performed to learn the structural properties of the potential products (mainly for olefins) formed in DDR zeolite, and the Ground state structures of these compounds were fully relaxed with PBE0 functional theory.\textsuperscript{172} The kinetic diameters of these molecules were calculated from the optimized molecular structures and further corrected with the van der Waals radii of outer-most atoms (as shown in Table 4.4).\textsuperscript{173-176} Compared to the pore size of DDR zeolite (3.6 × 4.4 Å), large olefins (like cis-2-butylene, trans-2-pentene) are easily confined inside of the catalyst. This property of DDR zeolite is also widely used for the gas separation, and here it plays a very important effect on the product distribution during the MTO reaction (as shown in Scheme 4.1). In the olefins-based catalytic cycle, light olefins methylate or oligomerize to form higher olefins. But with the transport restrictions, these higher olefins are confined inside of DDR catalyst and then subsequently undergo β-scission to form light olefins, predominately propylene. And finally, the enhanced propagation of the olefins-based catalytic cycle results in higher selectivity toward propylene, while the enhanced propagation of the aromatics-based catalytic cycle leads to higher ethylene selectivity, as observed experimentally.
Table 4.4. The calculated kinetic diameters of the potential products.

<table>
<thead>
<tr>
<th>Products</th>
<th>Kinetic Diameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>3.83</td>
</tr>
<tr>
<td>Ethylene</td>
<td>3.90</td>
</tr>
<tr>
<td>Propylene</td>
<td>4.45</td>
</tr>
<tr>
<td>Propane</td>
<td>4.33</td>
</tr>
<tr>
<td>trans-2-butylene</td>
<td>4.47</td>
</tr>
<tr>
<td>cis-2-butylene</td>
<td>4.91</td>
</tr>
<tr>
<td>trans-2-pentene</td>
<td>4.63</td>
</tr>
<tr>
<td>2-methyl-2-butylene</td>
<td>5.52</td>
</tr>
<tr>
<td>trans-2-hexene</td>
<td>4.86</td>
</tr>
<tr>
<td>2-methyl-2-pentene</td>
<td>5.52</td>
</tr>
<tr>
<td>2-methyl-2-hexene</td>
<td>5.53</td>
</tr>
</tbody>
</table>
Scheme 4.1. Catalytic conversion of methanol on DDR-type zeolite via the aromatics-based (left) and the olefins-based (right) catalytic cycles.

4.4 In conclusion

The role of olefins-based catalytic cycle and its influence on propylene selectivity was demonstrated in the methanol to olefins reaction over small-pore DDR zeolite. By the systematically investigation on the MTO performance of different structured DDR samples, we demonstrate the role of olefins-based catalytic cycle in the MTO conversion over small-pore zeolite. For MTO reaction at 45 – 55% methanol iso-conversion on investigated DDR zeolites, ethylene selectivity decreased monotonically from 36.6 % to 27.8 % at 400 ºC and from 46.2 % to 37.9 % at 450 ºC, while propylene selectivity increased monotonically from 38.1 % to 48.3 % at 400 ºC and from 36.4 % to 41.1 % at 450 ºC as Si/Al increased from 22 to 172. In DDR sample with shorter diffusion length, the selectivity toward propylene was further increased to 50.6 % at 400 ºC and 43.6 % at 450 ºC. And results from $^{12}$C/$^{13}$C methanol switch experiments and the analysis on
remained species in used catalysts demonstrate that with the preferential propagation of olefins-based catalytic cycle, the selectivity toward propylene is promoted accordingly. The mechanistic basis is that due to the transport restrictions, the higher olefins are confined inside of the DDR catalyst and then subsequently undergo β-scission to produce propylene predominately. This work provides new insights on the role of olefins-based catalytic cycle and extends the concepts of dual-cycle mechanism for MTO reaction over small-pore zeolite catalysts.
Chapter 5: Oxygen-containing coke species in zeolite-catalyzed conversion of methanol to hydrocarbons

5.1 Introduction

The reaction of MTH allows for the production of fuels and important building blocks for the chemical industry (like propylene, ethylene, and BTX) from carbon-based feedstocks through a syngas route, circumventing the dependence on petroleum-based synthetic routes. Due to the strong Brønsted acidity and microporous crystalline structure giving rise to high catalytic activity and unique shape selectivity, zeolites are the most important catalysts for MTH reaction. A vast literature are published for the mechanism of MTH conversion over various zeolites and on the effect of the zeolites’ pore structures on the product distributions. Over the last several decades, extensive research has shown that MTH reaction follows a generally accepted “hydrocarbon pool” mechanism with two competitively catalytic cycles, an aromatics-based cycle and an olefin-based cycle, coexisting in the process in which polymethylbenzenes (PMBs) and olefins act as the active hydrocarbon pool species, respectively, to produce the complex hydrocarbons through methylation, dealkylation, hydrogen transfer, and cracking reactions. This mechanism could help to explain the observed product distributions of MTH reaction for various zeolites by

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3 Portions of this chapter have been previously published: Catalysis of Science and Technology, 2016, 6, 8157-8165. Reproduced with permission of the Royal Society of Chemistry
considering the influence of the pore structures of zeolite catalysts on the relative propagation of these two cycles.

With equal importance to the activity or selectivity of a catalyst is the lifetime. Similar to many other hydrocarbon-based reactions, MTH conversion is also accompanied with the formation of coke, causing a gradual deactivation over the catalyst. Different from the thorough understanding of the mechanism which leads to the conversion of methanol to desired products (olefins or aromatics), much less is known on the coke formation and the consequent deactivation of the catalyst during MTH conversion. The formed coke is really complex in composition, which is mainly consisted of various polycyclic aromatics with a broad mass distribution. These bulky aromatics are formed and evolved throughout the whole reaction process with a very close correlation to the reaction conditions. Due to this complexity together with the varied reaction conditions in different researches, inconsistent observations and conclusions regarding the coke formation in MTH reaction have been provided. Some seemingly simple questions remain controversial, such as where is the preferential coke formation region in the zeolite crystals (outer surfaces vs. inner channels) and how does the catalyst deactivation take place (acid sites blocking vs. pore entrance blocking).

Very recently, Müller and coworkers investigated the process of coke formation and deactivation over ZSM-5 during the MTH reaction. By comparing the deactivation behavior of the catalyst in different plug-flow and fully back-mixed reactors, they claimed that, in the initial time of the MTH reaction, high local methanol concentration
can induce the formation of oxygen (O)-containing species which are strongly adsorbed on the Brønsted acid sites, leading to a rapid deactivation of catalyst; with time going on, these O-containing species are transformed to larger aromatic compounds and thus finally to the typical coke species (i.e. polycyclic aromatics). They proposed that these O-containing species deactivate the catalyst more severely than the subsequently formed coke species owing to the different deactivation mechanisms: blocking the active sites by chemisorption vs. blocking the pore structures by steric hindrance. With this work, they clearly explained the different deactivation kinetics of the catalyst observed in the different reactors. More importantly, they pointed out the crucial role of O-containing species in deactivating the catalyst during the MTH conversion. However, they didn’t identify any specific O-containing species experimentally, although they speculated that furan was one possible candidate.

We independently discovered the presence of O-containing species in the coke after the MTH conversion, when we examined the deactivated Beta zeolite catalysts by EELS (electron energy loss spectroscopy). Furthermore, we also successfully identified one O-containing compound (i.e. 4-methyl-benzaldehyde), from the soluble coke species. Our result is in agreement with Müller et al.’s hypothesis very well, and our definitive identification of O-containing species could allow us to investigate the influence on the reaction pathways and on the catalyst deactivation.

In this chapter, we investigated the influences of oxygen-containing compounds on coke formation, catalyst deactivation, product selectivity, and the induction period of the
MTH conversion. First, we found that the types of O-containing compounds are closely related to the pore structures of zeolites, very interestingly. And then, with ZSM-5 as a model catalyst, we investigated its influence on the MTH reaction by co-feeding the identified O-containing compound together with methanol. Our findings show that the presence of this compound can suppress the conversion of methanol, expedites the coke formation, and deactivates the catalyst. With a minor effect, the aromatics-based cycle of MTH reaction is enhanced meanwhile. Density functional theory (DFT) calculations reveal that in comparison with the co-existed species, O-containing compound is preferentially adsorbed on Brønsted acid sites, in which it can easily transform to large aromatics and bulky coke species.

5.2 Experimental section

5.2.1 Materials

Zeolite ZSM-5 with Si/Al = 25 in ammonium form was purchased from the company of Alfa Aesar. The ammonium form zeolite was transformed to hydrogen from via a process of calcination in air at 550 °C for 5 h, and it was designated as H-ZSM-5. Beta zeolite samples were synthesized based on previously published methods.\textsuperscript{126,132}

5.2.2 Catalytic reactions

MTH reactions were performed in a quartz fixed-bed reactor (the size is 8 mm in diameter) packed with zeolite catalysts. Prior to each run, the catalyst beds were activated under 50 mL/min pure N\textsubscript{2} flow at 550 °C for 60 min, after which the temperature was down to 330 °C, and the gas flow was switched to 50 mL/min N\textsubscript{2} gas
flow mixed with the desired feedstock induced by a high pressure HPLC pump to control the flow rate. In co-feeding experiments, the main substrate methanol was pre-mixed with one O-containing compound (2, 3-dimethyl-2-cyclopenten-1-one) or toluene according to a desired weight ratio. In experiments with the test of catalysts’ lifetime, the weight hourly space velocity (WHSV) was adjusted to ~19 g_{feed}·g_{Cat}^{-1}·h^{-1}. In experiments to investigate the product distribution as a function of contact time, the WHSVs were then adjusted among ~76 to ~237 g_{feed}·g_{Cat}^{-1}·h^{-1}. In experiments to investigate the induction period of the reaction, the temperature was set at 245 °C, and the WHSV was adjusted to 3.8 g_{feed}·g_{Cat}^{-1}·h^{-1}. All of the reactions were performed at atmospheric pressure, with the product analyzed by an online GC (gas chromatography). Analysis on the composition of effluent was carried out by GC with a flame ionization detector (FID) which was equipped with an Agilent HP-PLOT/Q column (30 m*0.53 mm*40 μm).

5.2.3 Analysis of the coke species in used catalysts

In order to determine the total coke amount of the used catalysts, a Netzsch TG 209 F1 TGA (thermogravimetric analysis) machine was performed with the temperature increased from 150 °C to 850 °C at a constant temperature ramping rate of 10 °C/min, and under an air flow with a rate of 25 mL/min. The residual soluble organic species inside of the catalysts were first extracted following by a commonly used HF-based procedure.\textsuperscript{101-102, 133} In details, the catalyst was first taken out from the reactor after a desired reaction time, and then 200 mg of the used catalyst was transferred to a capped
Teflon vial and dissolved in 6 mL 24% HF for 3 h. And, 6.0 mL CH₂Cl₂ was then added to the solution in order to extract the liberated organic species from the original water phase. With about 3 h, this organic phase was finally separated from the original liquid mixture and tested on GC and GC–MS which were equipped with a same HP-5 Agilent column (30 m*0.32 mm*0.25 μm).

5.2.4 DFT calculations

The Brønsted acid sites in protonated H-ZSM-5 zeolite were modeled by a 128T cluster truncated from the lattice structure of corresponding zeolites. The clusters were terminated by H atoms bonded to Si atoms, with the terminal Si–H bond length fixed at 1.47 Å. The Al atoms associated with the Brønsted acidity were introduced at the most plausible position. All of the calculations were then performed with the generally accepted ONIOM approach as implemented in the GAUSSIAN 09 Package. In this method, density functional theory (DFT)-based calculations at the B3LYP/6-31G (d,p) level were applied to the inner 14T cluster, which was considered to represent the active region of zeolite, including the 10-membered ring in ZSM-5 zeolite, with additional basal T units to keep the unity of the Brønsted acid sites. The remained part of the cluster was treated with the universal force field (UFF). During optimization, only the 14T active region, [(≡SiO)₃Al(OH)Si≡] and the adsorbates were allowed to relax, whereas the rest of the cluster model was fixed at the crystallographic coordinates. The transition states were located with the Berny algorithm in redundant internal
coordinates and each transition state was confirmed by frequency analysis with only one imaginary frequency along the corresponding reaction direction.192-194

5.3 Results and discussion

5.3.1 The detection of O-containing compounds

The MTH reactions over zeolite catalysts were performed in a fixed-bed reactor at 330 °C. The details of the MTH reaction conditions are elaborated in 5.2.2 experimental section. After the catalysts were deactivated at conversions lower than 10 %, we stopped the reactions, collected the catalysts from the fixed-bed, and extracted the organic species retained in the spent catalysts via the standard method, dissolution of the aluminosilicate framework by HF solution followed by the extraction of organic species with CH2Cl2 from the water phase.101-102, 133 The soluble species were then analyzed via GC and GC–MS. These results show that exception of the common hydrocarbons, i.e. various PMBs and bulky olefins (C10-C14), O-containing compounds also exist in the spent catalysts. Specifically, 2, 3-dimethyl-2-cyclopenten-1-one and 2, 3, 4-trimethyl-2-cyclopenten-1-one were found in ZSM-5 (Figure 5.1 & Figure 5.2). We then conducted MTH reactions with 13C-MeOH used as the feed in this project. As shown in the mass spectrometric data (Figure 5.2), these isotopic experiments clearly demonstrate that all the carbon atoms in these two compounds are originated from the methanol feed. In details, the observed 2,3-dimethyl-2-cyclopenten-1-one in the case of 13C-MeOH shows a mass of 117, compared to that one (m= 110) obtained from 12C-
MeOH feed. Likewise, substituting $^{13}$C-MeOH for $^{12}$C-MeOH leads to an increase in the mass of 2,3,4-trimethyl-2-cyclopenten-1-one from 124 to 132.

![Chemical structures and GC-MS profile](image)

**Figure 5.1.** Oxygen-containing compounds identified in coke from MTH conversion formed in zeolite catalysts: (a) 2, 3-dimethyl-2-cyclopenten-1-one, (b) 2, 3, 4-trimethyl-2-cyclopenten-1-one, and (c) 4-methyl-benzaldehyde. (a) and (b) were identified from zeolite H-ZSM-5 and (c) was identified from zeolite H-Beta. (d) The GC-MS elution profile of the residual soluble coke species extracted from the used H-ZSM-5 catalyst. The inset shows the enlarged region of retention time of 10-20 mins, where 1* and 2* label 2, 3-dimethyl-2-cyclopenten-1-one and 2,3,4-tri-methyl-2-cyclopenten-1-one, respectively.
Figure 5.2. (a) MS spectra of the extracted O-containing compound, 2,3-dimethyl-2-cyclopenten-1-one, from different feeds: $^{12}\text{C-MeOH}$ (top) and $^{13}\text{C-MeOH}$ (bottom). (b) MS spectra of the extracted O-containing compound, 2,3,4-trimethyl-2-cyclopenten-1-one, from different feeds: $^{12}\text{CMeOH}$ (top) and $^{13}\text{C-MeOH}$ (bottom)

The O-containing compounds (hereafter designed as oxygenates) were detected only in the coke deposited in spent catalyst but not in the effluent products during the MTH reaction. We subsequently infer that once they are produced, these oxygenates could strongly adsorb on the active acid sites of the catalysts and/or they quickly transform into other hydrocarbon products. Actually, we could only observe marked GC-MS signals of these oxygenates when we examined a highly concentrated solution of the soluble species. This shows their low contents respect to the other species in the spent catalyst, which may be the reason they were always overlooked in previous researches. This observation of the oxygenates was reproduced in repeated experiments, confirming
that they are produced during the MHT conversion as intermediates rather than from accidental experimental error or contamination.

5.3.2 The influence of O-containing compounds on the deactivation of catalyst

Even though it is a little difficult to explore the formation pathway of these oxygenates species from methanol conversion, we can also investigate how they affect the deactivation process of the zeolite catalysts and the product distributions by co-feeding them with methanol during the MTH reaction. The process of co-feeding is commonly used way to probe the role of the various intermediates during the MTH reaction. For example, toluene and propene were co-fed with methanol to promote the propagation of the aromatics-based cycle and olefins-based cycle, respectively, which provided strong evidences for the dual-cycle mechanism.\textsuperscript{65, 87} In this chapter, we co-fed 2, 3-dimethyl-2-cyclopenten-1-one (denoted as CP) with methanol over ZSM-5 zeolite for the MTh reaction. In a comparing experiment, we used toluene as an alternative co-feeding compound with methanol and kept other conditions all identical for the comparison purposes.

Figure 5.3 depicts the evolution of the conversion of methanol as a function of time-on-stream for the three feedstocks: methanol, methanol co-fed with 5 wt% CP, and methanol co-fed with 5 wt% toluene. At a weight hourly space velocity (WHSV) of \(~19\ g_{\text{Feed}}\cdot g_{\text{Cat}}^{-1}\cdot h^{-1}\) and a reaction temperature of 330 °C, the very initial conversion of methanol was all 100% in these three systems. With a prolonged time on stream, however, a significant difference in the lifetime of the catalysts was observed clearly.
With the methanol as the feed alone, the conversion of methanol was retained at a conversion of 100 % for about 5 h later and then gradually dropped to ~40 % at the time of 10 h. When co-feeding with 5 % toluene, it did not significantly accelerate the deactivation rate of the ZSM-5 catalyst (Figure 5.3). In a sharp contrast, however, co-feeding with 5 wt% CP gave rise to a very rapid decrease in the methanol conversion to about 20 % within only 4 h (Figure 5.3). Given that the deactivation of catalyst is most likely caused by coke formation, this data suggest that co-feeding CP with methanol can efficiently lead to the formation of bulky coke species. Hence, we then examined the coke contents in the spent catalysts using TGA technique, according to the weight loss from 150 °C to 850 °C (Figure 5.4). The results clearly show that co-feeding CP with methanol indeed leads to a quick coke formation. Specifically, 4.6 wt% coke (relative to the mass of the ZSM-5 catalyst) was only produced after 1 hour of the MTH reaction with methanol as the feedstock, while 6.9 wt% coke was formed under the very same conditions with the feedstock of methanol co-fed with 5 % CP, corresponding to a 50 % increase in the coke formation rate (Figure 5.4). We also measured the coke contents in the spent catalysts with a prolonged time on stream (i.e. 10 h for methanol alone as the feed and 4.5 h for methanol co-fed with CP as the feed), when the catalysts were both largely deactivated with less than 40 % conversion of methanol. The result that the coke contents are comparable in these two cases (9.7 wt% vs. 10.3 wt%) confirms that the faster coke formation was associated with CP species, and also directly correlates the loss of the catalyst activity with the content of coke formed (Figure 5.4).
Figure 5.3. Catalytic lifetime of the H-ZSM-5 catalyst in MTH reactions at 330 °C and a WHSV of ~19 $\text{g}_{\text{Feed}} \cdot \text{g}_{\text{Cat}}^{-1} \cdot \text{h}^{-1}$ with different feedstocks: pure methanol, methanol co-fed with 5 wt% toluene, and methanol co-fed with 5 wt% CP.

Figure 5.4. TGA profiles of coked H-ZSM-5 catalysts with different feedstocks (pure methanol and methanol co-fed with 5 wt% CP) and reaction times as labeled. The weight losses indicated in the figure correspond to the coke contents.
5.3.3 The influence of O-containing compounds on the product distribution

In prior studies of MTH, ethylene selectivity and higher aliphatics (e.g., C₄–C₇) selectivity were often used as indicators of the degree of propagation of the aromatics-based cycle and the olefins-based cycle, respectively (schemes are shown in the references).¹⁷, ⁶⁵, ¹²⁹ It has also been reported that co-feeding methanol with PMBs (e.g., toluene) can largely promote the aromatics-based cycle, as evidenced by the increased ethylene production.⁶⁵, ⁸⁷ Our finding that co-feeding CP with methanol gave rise to a quick formation of coke inspired us to study whether CP species has a similar effect as that of toluene on the propagation of the aromatics-based cycle, given that the formation of coke involves the aromatics as the intermediates.¹⁰⁴ Figure 5.5 presents the conversion of methanol and the selectivity to ethylene and aliphatics C₄–C₇ at varied contact times with different feedstocks. We observed that in a good agreement with the previous literature,⁶⁵ co-feeding methanol with toluene promoted the aromatics-based cycle selectively, leading to a higher methanol conversion, an increased selectivity toward ethylene from ~12 % to ~17 %, and a decreased selectivity to C₄–C₇ aliphatics from ~45 % to ~35 % (Figure 5.5). In comparison, co-feeding methanol with CP had a similar but less remarkable effect on methanol conversion and product distribution (~13% for ethylene and ~40% for C₄–C₇ aliphatics) (as seen in Figure 5.5). There was an exception observed at a short contact time (i.e., 10 min·g_cat/mol_MeOH), when co-feeding methanol with CP gave rise to a much lower methanol conversion respect to the other two cases (Figure
indicating a severe deactivation of the catalyst by a relatively high concentration of CP.

**Figure 5.5.** Conversions (a), ethylene selectivity (b), and C₄-C₇ aliphatics selectivity (c) as functions of contact time on H-ZSM-5 with different feedstocks: pure methanol, methanol co-fed with 5 wt% toluene, and methanol co-fed with 5 wt% CP. The reactions were carried out at 330 °C and 20 min time on stream.
5.3.4 The influence of O-containing compounds on the induction period

It is well known that by adding a small amount of the active intermediates, such as toluene, in the methanol feedstock can significantly shorten the induction period of MTH reactions.\textsuperscript{16, 50, 195-196} If CP can act as or be easily converted to the active intermediates for MTH conversion, co-feeding CP with methanol would also help to shorten the induction period. Hence, we then investigated the influence of co-feeding methanol with CP on the induction period in comparison with feeding the pure methanol and co-feeding methanol with toluene. We decreased the reaction temperature to 245 °C to extend the induction period for an easy comparison.\textsuperscript{50} Figure 5.6 indicates that at this low reaction temperature, the conversion of methanol was indeed retarded; the conversion was as low as 1.5% after 250 min of reaction when the feedstock was pure methanol. When 0.1 wt% toluene was co-fed with methanol, the induction period was markedly shortened, showing a methanol conversion of 14 % at only 50 min. The reason is that toluene is one of the important hydrocarbon pool species and thus its addition facilitates the initiation of the catalytic cycles.\textsuperscript{50} In comparison, adding 0.12 wt% CP (the same amount of C as the case of co-feeding 0.1 wt% toluene with methanol) into methanol only slightly promoted the MTH reaction, leading to a methanol conversion of 3 % at 200 min (Figure 5.6). These data show that with respect to toluene, which is a direct hydrocarbon pool species, CP is less efficient in promoting the MTH reaction. We noticed that the addition of CP in the feed did not enhance but rather suppressed the conversion of methanol during the first 30 min of
MTH reaction, while a slight enhancement emerged after 50 min (Figure 5.6). This can be attributed to that CP and methanol are first competitively chemisorbed on the Brønsted acid sites (BASs) of the catalyst and then the subsequent conversion of CP to aromatic intermediates caused the boost in methanol conversion.

![Graph](image)

**Figure 5.6.** Conversion of methanol as a function of time on H-ZSM-5 at 245 °C and a WHSV of 3.8 \( \frac{g_{\text{Feed}}}{g_{\text{Cat}} \cdot h^{-1}} \) with different feedstocks: pure methanol, methanol co-fed with 0.1 wt% toluene, and methanol co-fed with 0.12 wt% of CP.
Taken together, these results all indicate that the production of CP has two effects on MTH reaction: the minor one is improving the aromatics cycle; the major one is causing the formation of coke and thus the deactivation of catalyst. We hypothesize that once it is produced, CP molecule is preferentially chemisorbed on the BASs, preventing the adsorption and thus suppressing the conversion of methanol. The adsorbed CP molecule is rapidly transformed into large aromatic species, which remain chemisorbed on the BASs with a very low tendency to enter into the aromatics cycle; on the contrary, they tend to grow into coke species with high molecular weight, possibly through the process of methylation reaction.

### 5.3.5 DFT calculation on the adsorption energy of active species on acidic site

In order to validate our hypothesis, we calculated the adsorption energy ($E_{\text{ad}}$) of various substrates and intermediates including methanol (MeOH), dimethyl ether (DME), ethylene (ET), CP and benzene (BZ), on the BASs of ZSM-5 via the ONIOM approach as implemented in the GAUSSIAN 09 Package. We didn’t investigate the adsorption of longer olefins, heavy aromatics and their derivatives as they would behave similarly to ethylene and benzene. The most plausible adsorption configurations are summarized in Figure 5.7. Based on the calculations, reactant MeOH can form two hydrogen bonds with the ZSM-5 framework (Figure 5.7a), where the distance between the O of MeOH and the framework proton of ZSM-5 is 1.41 Å, and the distance between the H of hydroxyl group of MeOH and the neighboring bridge O in ZSM-5 is 1.75 Å. As a consequence, the adsorption energy $E_{\text{ad}}$ of MeOH adsorbed on ZSM-5 is as high as -
135.75 kJ/mol. DME can form one hydrogen bond with ZSM-5 using the ether O (Figure 5.7b). Its $E_{\text{ad}}$ was calculated to be -115.07 kJ/mol. The charge-abundant C atom of ET interacts with the zeolite framework proton to form a π complex with an $E_{\text{ad}}$ of -60.68 kJ/mol (Figure 5.7c). The intramolecular charge delocalization of BZ results in the nearest C(BZ)-H distances of 2.24 Å (Figure 5.7d), with an $E_{\text{ad}}$ of -70.28 kJ/mol. The CP molecule is oriented to maximize its interaction by its oxygen with the BAS at an O-H distance of 1.57 Å. This interaction and the associated charge transfer alter the conjugation among the π states delocalized along the backbone with the elongation of the C=O (from 1.22 to 1.23 Å) and C=C (from 1.36 to 1.37 Å), and O(ZSM-5)-H (from 0.96 to 1.01 Å) for formation of a positively charged enol-like structure at the BAS, which in turn effectively stabilize the adsorption structure (Figure 5.7e). Consequently, CP has the highest $E_{\text{ad}}$ (-173.16 kJ/mol) among all the explored compounds. This data support our hypothesis that CP molecule can preferentially chemisorb at the BASs over the co-existing reactants and intermediates during the MTH conversion. The result also explains the suppression of the reaction which was observed in the co-feeding experiments with a high CP concentration (Figure 5.5a) or at the initial stage of the MTH reaction (Figure 5.6).
Figure 5.7. The most plausible configurations for the absorption of MeOH (a), DME (b), ET (c), BZ (d), and CP (e) on the BAS of H-ZSM-5. The zeolite framework is presented in the form of a wireframe with the exception of the inner 14-T atoms and the bridging O atoms that are presented using ball-and-stick models along with the adsorbed molecules (gray-silicon, red-oxygen, pink-aluminum, and white-hydrogen). The calculated adsorption energy of each molecule is listed on the bottom right.

On the basis of our experimental results and DFT calculations, we propose the reaction pathways to illustrate how the identified oxygenates influence MTH conversion, as exemplified using CP (Scheme 5.1). The proposed reaction pathways start from the adsorbed CP on BASs, because of that we currently don’t understand how these oxygenates are formed from methanol. Despite the large size of CP that may hinder its direct reaction with the co-existing species in the confined zeolite channels, it can undergo isomerization from a cyclic ketone to an enol. The hydroxyl group of enol is protonated on the BAS sites, followed by dehydration to form an adsorbed cyclic C₅-
carbenium (scheme 5.1). Similar C₅-carbenium intermediates have been observed in MTH conversion.¹⁹⁷ The dehydration on this path is endothermic by 74.30 kJ/mol and would be facile in the MTH environment. The resulting C₅-carbenium ion undergoes ring opening and rearrangement reactions to form a methyl-cyclohexadiene (scheme 5.1). The energy change for this step is calculated to be only 13.13 kJ/mol. The methyl-cyclohexadiene can be cracked to release methane, leaving C₆-carbenium ion at the BAS. As indicated by Müller et al.,¹⁰⁰ unlike the typical hydrogen transfer reaction between two olefins that restores the BAS and produces free aromatics to readily participate in the MTH catalytic cycle, this reaction pathway results in the formation of aromatic species (C₆-carbenium ion) strongly chemisorbed at the BAS in which they can further grow into higher-molecular-weight coke species (Route I, Scheme 5.1). Thus, both the blocking of acid sites by CP and its derivatives and the subsequent coke formation accounts for the catalyst deactivation. Alternatively, free toluene can be released from the methyl-cyclohexadiene along with the restoration of the BAS (Route II, Scheme 5.1), leading to a slight enhancement of the aromatics-based cycle which was observed in our experiment. Our calculations indicate that route I is about 10 kJ/mol more exothermic with respect to route II.
Scheme 5.1. Proposed adsorption and conversion pathways of CP on the acid sites of zeolite.

5.4 Conclusion

We discovered trace amounts of oxygen-containing compounds in the coke formed during the MTH reactions over zeolite catalysts. This finding suggests that these compounds may participate in MTH conversion as intermediates. Although the presence of oxygenates during MTH conversion was previously hypothesized, the successful identification of these compounds allowed us to investigate their direct influence on MTH conversion. We demonstrated that the presence of such a compound suppresses the conversion of methanol by prior adsorption on the acid sites of the zeolite, where it can be rapidly converted to aromatics and coke species. As such, these O-containing compounds play crucial roles in deactivating the catalyst by site blocking followed by coke formation. In addition, the conversion of O-containing compounds to aromatics
can slightly enhance the aromatics cycle of the MTH reaction, leading to higher selectivity for ethylene. We suggest that with the means to manipulate the production of such O-containing compounds during MTH conversion, we could extend the lifetime of the catalyst and tune the product selectivity.
Chapter 6: Conclusions and outlooks

In conclusion, we prepared and investigated three series of different types of zeolites to gain fundamental understanding of the relationship between the structural parameters of zeolites and their catalytic performances in MTH reactions.

First, we synthesized mesoporous Beta zeolite and investigated the influence of mesoporosity on its catalytic performance for the conversion of MTH. In this work, we also prepared conventional microporous Beta-C zeolite for the comparison. Our findings show that the significant intra-crystalline mesoporosity is indeed advantageous for improving the accessibility of acid sites in the catalyst crystals, and thus give rise to a better performance (i.e. larger conversion capacity, faster conversion rate, and a remarkably longer catalyst lifetime). Much more importantly, the mesoporosity plays an important effect on the mechanism of MTH conversion. Methylbenzenes, the intermediates of the aromatic-based cycle, can easily diffuse out from the zeolite channels in mesoporous Beta, limiting the propagation of this catalytic cycle, while relatively promoting the olefin-based cycle. As a result, Beta-MS gave lower ethylene selectivity but higher selectivity towards C₄ – C₇ aliphatics with respect to Beta-C.

In the second work, we then studied the effect of aluminum content on ethylene selectivity in MTH conversion over series of ZSM-5 zeolites. In order to achieve this purpose, we prepared five ZSM-5 zeolites with similar crystallite sizes (150 – 240 nm) and varied Si/Al ratios between 55 and 1580. Our catalytic data show that the ethylene
selectivity, increased from 5.7% on ZSM-5 sample with low aluminum content (Si/Al = 1580) to 16% on ZSM-5 sample with high aluminum content (Si/Al = 55). These result coincides with the previous finding that ethylene selectivity increase with decreasing the crystallite size of ZSM-5, and these two observations can be explained by the same mechanistic reason, that is, the ethylene selectivity is associated with the propagation degree of the aromatics catalytic cycle and essentially determined by the number of the acid sites that methylbenzenes (MTH intermediates) would encounter before they exit the zeolite crystallite. Finally, a single-value parameter describes the combined effects of aluminum content and crystallite size on ethylene selectivity for MTH conversion on ZSM-5 zeolite.

In the third work, we focused on the role of olefins-based catalytic cycle and its influence on propylene selectivity in the methanol to olefins (MTO) reaction over small-pore DDR zeolite. For MTO reaction at 45 – 55% methanol iso-conversion on investigated DDR zeolites, ethylene selectivity decreased monotonically from 36.6 % to 27.8 % at 400 °C and from 46.2 % to 37.9 % at 450 °C, while propylene selectivity increased monotonically from 38.1 % to 48.3 % at 400 °C and from 36.4 % to 41.1 % at 450 °C as Si/Al increased from 22 to 172. In DDR sample with shorter diffusion length, the selectivity toward propylene was further increased to 50.6 % at 400 °C and 43.6 % at 450 °C. And results from $^{12}$C/$^{13}$C methanol switch experiments and the analysis of remained active species in used catalysts demonstrate that with the preferential propagation of olefins-based catalytic cycle, the selectivity toward propylene is
promoted accordingly. The mechanistic basis is that due to the transport restrictions, the higher olefins are confined inside of the DDR catalyst and then subsequently undergo β-scission to produce propylene predominately.

With these researches, we finally hope to offer some constructive guidance or advice on the catalysts design for high valuable products in MTH conversion. As illustrated in Scheme 6.1, based on our gained insights from our work, we can get these outlooks as follows:

if we want to gain ethylene as the main product in MTH reaction, we have to enhance the propagation of aromatics-based cycle by increasing the hydrogen transfer process and restricting the diffusion of aromatics, and thus a zeolite with low Si/Al ratio and large crystallite size is needed; if we want to gain propylene as the main product in MTH reaction, we have to enhance the propagation of olefins-based cycle by decreasing the hydrogen transfer process and restricting the diffusion of olefins, and thus a zeolite with high Si/Al ratio and small pore size is needed; if we want to gain aromatics as the main products in MTH reaction, we have to increasing the hydrogen transfer process and promoting the diffusion of aromatics, and thus a zeolite with high Si/Al ratio and small crystallite size are needed.
### Scheme 6.1

Constructive guidance on catalysts design for high valuable products in MTH conversion based on our research.

<table>
<thead>
<tr>
<th>Target Product</th>
<th>Effective Method</th>
<th>Catalyst Design</th>
</tr>
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<tbody>
<tr>
<td>Ethylene</td>
<td>Enhance the aromatics-based cycle, (increase the hydrogen transfer process and restrict the diffusion of aromatics)</td>
<td>Low Si/Al ratio and large crystallite size</td>
</tr>
<tr>
<td>Propylene</td>
<td>Enhance the olefin-based cycle, (limit the hydrogen transfer process and restrict the diffusion of large olefins)</td>
<td>High Si/Al ratio and small pore size</td>
</tr>
<tr>
<td>Aromatics</td>
<td>Increase the hydrogen transfer process, and promote the diffusion of aromatics</td>
<td>Low Si/Al ratio and small crystallite size</td>
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</tbody>
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